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April 15, 2013

Mr. Tien Q. Duong
EE-2G/Forrestal Building
Office of Vehicle Technologies
U.S. Department of Energy
1000 Independence Avenue, S.W.
Washington D.C. 20585

Dear Tien,

Here is the first quarter FY 2013 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from http://batt.lbl.gov/reports/quarterly-reports/.

Sincerely,

Venkat Srinivasan
Acting Head
BATT Program

edited by: V. Battaglia
M. Foure
S. Lauer

cc:

J. Barnes	DOE/OVT
P. Davis	DOE/OVT
D. Howell	DOE/OVT
J. Muhlestein	DOE-BSO

FEATURED HIGHLIGHTS

Anodes–

- **Kumta's Group produces Si-nanotubes capable of 2000 mAh/g of stable cycling performance at C/1 rate.**

Electrolytes –

- **Angell's Group shows good cycleability of the high-voltage Ni-spinel material in a sulfone based eelctrolyte.**

Cathodes–

- **By performing their synthesis inside a syncrotron and taking X-ray data in real time, Looney and Wang were able to determine a synthesis root for making a 300 mAh/g Cu-V-O compound.**

Diagnostics –

- **Collaborative research in the Ni-spinel Focus Group leads to:**
  - **Chen and Kostecki demonstrate that octohedron cycle better with less side reactions and a more table SEI than platelets.**
  - **Cabana demonstrating that the disordered material starts with a solid solution phase before transforming to a two phase material where the ordered material does not. This may explain higher rate capability of disordered material**
  - **Yang and Nam show that the ordered material is more stable to thermal decomposition than the disordered material.**
  - **Persson predicts the most stable stuctures for the ordered and disordered material.**

- **Balsara obtains simulated XRD patterns for different Li_xS compounds in tetraglyme.**

BATT TASK 1

ELECTRODE ARCHITECTURE

Task 1.1-PI, INSTITUTION: Vincent Battaglia, Lawrence Berkeley National Laboratory

TASK TITLE: Electrode Architecture ─ Cell failure: electrochemical diagnostics

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Energy density of today's batteries is not high enough; cyclability is not high enough; calendar life is not long enough.

OBJECTIVE: To accurately assign the primary sources of energy and power fade of prominent chemistries and electrode designs that lead to advanced Li-ion technologies.

GENERAL APPROACH: Identify critical technology pathway to meet the USABC performance, life, and cost targets; and then identify cross-cutting failure modes of battery materials and electrodes that prevent the attainment of those goals. Design experiments and hardware that will provide fundamental insight into the problems. Materials from credible battery suppliers of a chemistry of particular interest to the BATT Program are procured. Electrochemical experiments are designed to draw out the identified problem. Additional hardware capable of extracting critical data is also designed, developed, and implemented.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. The presently accepted mechanism, based on an acidic, aqueous solution is suspect in the aprotic solvents found in Li-ion cells. Preliminary experiments suggested that the loss of Mn may be driven by the oxidation of electrolyte decomposition products and not by reduction reactions driven by the presence of protons.

The three-electrode cell hardware can be modified such that the third electrode can be substituted with a tube. The present hardware is not showing satisfactory sensitivity. The source of an inductance loop in the ac-impedance is presently unknown.

EXPECTED STATUS SEP. 30, 2013: The loss of Mn from a commercial Mn-spinel cathode material, as a function of voltage, temperature, and time, will be measured. The loss of Mn in the presence of a $LiPF_6$-based electrolyte will be compared to the loss of a LiTFSI-based electrolyte. The gas-sensing hardware for a coin cell will be verified while cycling. The source of the inductance loop in a 3-electrode coin cell, as identified by the Modeling Group, will be validated.

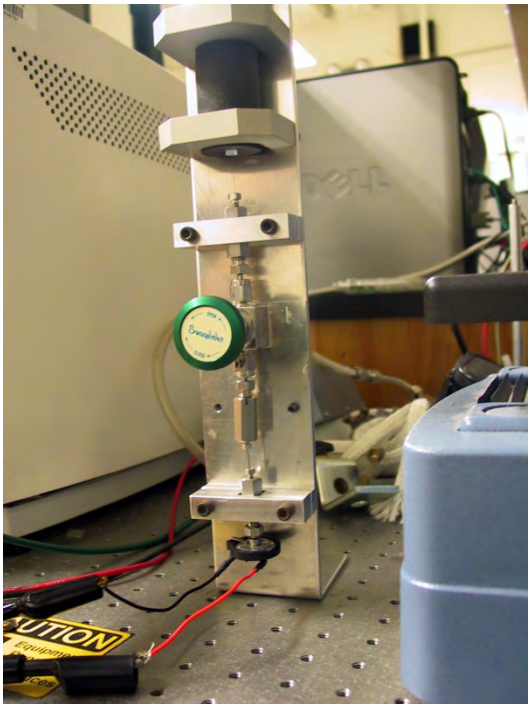
RELEVANT USABC GOALS: 200 to 300 Wh/kg; 1000 to 5000 full cycles; 10- to 15-year calendar life

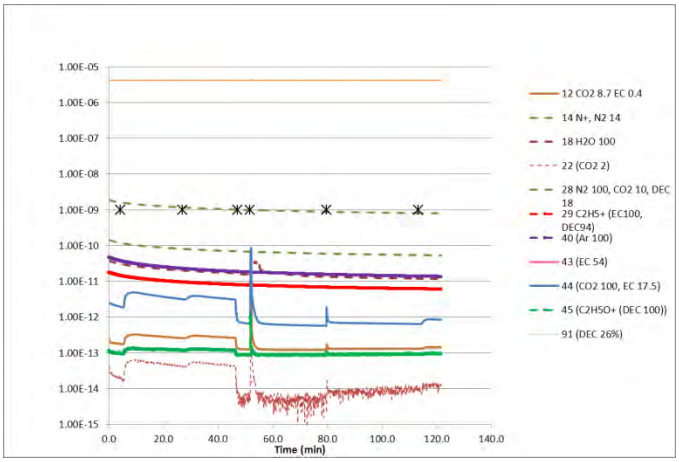
MILESTONES:

(a) Make a modification to the three-electrode cell hardware based on guidance from Modeling Group and measure difference in response. (May 13) **On schedule**
(b) Demonstrate gas-sensing apparatus for a coin cell on full cell. (Jun. 13) **On schedule**
(c) Measure potential dependence of Mn loss from Mn-spinel. (Jun. 13) **On schedule**

PROGRESS TOWARDS MILESTONES

(b) Gas-sensing apparatus for a coin cell demonstrated on full cell, June 2013. **On schedule.**
This quarter, a cell originally designed to hold a reference electrode was further modified, this time to hold a tube. The tube was then attached to our mass spectrometer. The idea is to be able to cycle a Li-ion cell, detect the gas, and measure its composition at the same time. The configuration is shown in the picture below, left.

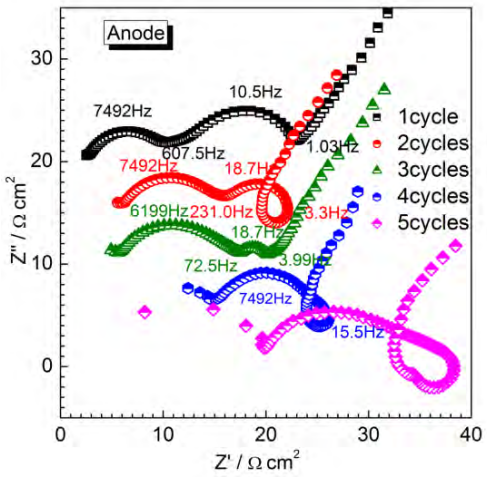




The figure above shows the output of our mass spectrometer after a series of events, which were performed with the cell removed from the apparatus. These events included: breathing into the valve tip, removing the valve, breathing into the line, reinstalling the valve, and breathing into the valve again. As a result of all of these tests, one sees that there is just one spike in the CO_2 reading, which occurred when the valve was removed and someone exhaled directly into the line.

This data suggests that the valve contains too much head space. Therefore, valves with minimum head space have been ordered to correct this issue. There may also be challenges regarding head space in the coin cell itself that may also need to be addressed. This can be optimized by experimenting with internal cell components.

(a) Make a modification to the three electrode cell hardware based on guidance from Modeling Group and measure difference in response, May 2013. **On schedule**.
A 3-electrode cell has been developed, but as can be seen in the figure to the right. The impedance measurement of the anode is drifting to the right with each cycle and there is an inductance loop that appears and disappears at around 4 Hz. It is presently believed that the shifting of the high-frequency intercept may be due to a disconnection of the reference form from the metal rod that extends through the cell. The Modeling Group is helping us understand the source of the inductance loop.



Task 1.2-PI, INSTITUTION: Karim Zaghib, Hydro-Québec (IREQ)

TASK TITLE: Electrode Architecture ─ Assembly of Battery Materials and Electrodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC).

BARRIERS: Low energy and poor cycle/calendar life

OBJECTIVE: To develop high-capacity, low-cost electrodes with good cycle stability and rate capability to replace graphite in Li-ion batteries.

GENERAL APPROACH: To address and overcome the electrochemical capacity limitations (both gravimetric and volumetric) of conventional carbon anodes, proposal is to develop low-cost electrode architectures based on silicon that can tolerate its volumetric expansion and provide an acceptable cycle life with low capacity fade. Volume expansion, which is a common problem with Si-based electrode materials, will be addressed by: i) tortuosity/porosity optimization, and ii) improved current collector technology.

STATUS OCT. 1, 2012: This is a new project initiated April 1, 2013.

EXPECTED STATUS SEP. 30, 2013: Complete the fabrication and testing of high-density Si-based electrodes with optimized tortuosity/porosity obtained by a dry-blended process. New current collector aarchitecture will be used to coat the Si-based anode. *In-situ* SEM and TEM analyses will be utilized to monitor the real-time change to the structure undergoing volume expansion. These analyses will help to understand the failure mode and to guide further improvements.

RELEVANT USABC GOALS: High energy and low cost: 96 Wh/kg (PHEV, 40 miles). Cycle life, calendar life: 15 year life (at 40°C).

MILESTONES:
(a) Identify an optimized dry-blended silicon-carbon powder composition. (Jun. 13) **On schedule**
(b) Optimize the architecture of the Si-anode and $LiMn_{1.5}Ni_{0.5}O_4$ cathode. (Sep. 13) **On schedule**
(c) Complete *in situ* SEM and TEM analyses of the optimized anodes. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.

Task 1.3-PI, INSTITUTION: Yet-Ming Chiang, Massachusetts Institute of Technology

TASK TITLE - PROJECT: Electrode Architecture – Design and Scalable Assembly of High Density Low Tortuosity Electrodes

SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF6+EC: DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Achieving sufficient electronic conductivity, achieving mechanical failure upon cycling, meeting automotive duty cycles, lowering cost.

OBJECTIVES: Develop scalable high density binder-free low-tortuosity electrode designs and fabrication processes to enable increased cell-level energy density compared to conventional Li-ion technology. Characterize electronic and ionic transport as a function of state-of-charge in relevant systems including $Li(Ni,Co,Al)O_2$ (NCA), Li_2MnO_3-$LiMO_2$ alloys and high-voltage spinels $LiM_xMn_{2-x}O_4$ and $LiM_xMn_{2-x}O_{4-y}F_y$.

GENERAL APPROACH: Fabricate high-density sintered cathodes with controlled pore volume fraction and pore topology. Test electrodes in laboratory half-cells and small Li-ion cells. Increase cell-level specific energy and energy density, and lower inactive materials cost, by maximizing area capacity (mAh/cm^2) at C-rates or current densities commensurate with operating conditions for PHEV and EV. Measure electronic and ionic transport in pure single-phase sintered porous electrodes while electrochemically titrating the Li concentration.

STATUS OCT 1, 2012: This is a new project initiated April 1, 2013.

EXPECTED STATUS SEP. 30, 2013: Complete directional freeze-casting and sintering process development for NCA electrodes. Complete measurement of electronic conductivity and Li diffusivity *vs*. *x* in sintered NCA. Complete pulse-power characterization tests on sintered LCO electrodes as a model material.

RELEVANT USABC GOALS: EV: 200 Wh/kg; 1000 cycles (80% DOD).

MILESTONES:

(a) Fabricate at least five NCA cathodes by directional freeze casting and sintering. (Apr. 13) **On schedule**

(b) Complete electrochemical testing of cathodes in (a), and complete measurement of electronic conductivity and diffusivity *vs*. *x* in sintered NCA. (Jun. 13) **On schedule**

(c) Complete measurement of electronic conductivity *vs*. *x* in sintered doped $LiM_xMn_{2-x}O_{4-y}F_y$. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.

Task 1.4-PI, INSTITUTION: Gao Liu, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Electrode Architecture – Hierarchical Assembly of Inorganic/ Organic Hybrid Si Negative Electrodes

SYSTEMS: High-voltage, high-energy: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC).

BARRIERS: High-energy system: poor cycle life, high first-cycle irreversible capacity, low coulomb efficiency.

OBJECTIVES: Enable Si as a high capacity and long cycle-life material for negative electrode to address two of the barriers of lithium-ion chemistry for EV/PHEV application - insufficient energy density and poor cycle life performance.

GENERAL APPROACH: The volume change of Si during lithiation and delithiation disrupts the integrity of electrode and induces excessive side reactions, leading to fast capacity fade. This work will combine material synthesis and composite particle formation with electrode design and engineering to develop high capacity, long-life, and low-cost hierarchical Si-based electrode. The research and development activity will provide an in-depth understanding of the challenges associated with assembling large volume change materials into electrodes, and will develop a practical hierarchical assembly approach to enable Si materials as negative electrodes in Li-ion batteries.

STATUS OCT. 1, 2012: New project initiated October 1, 2012.

EXPECTED STATUS SEP. 30, 2013: Understand the function of polarity in the binder performance using the triethyleneoxide (TEO) side-chain conductive binders; design and synthesize a series of alkyl-substituted vinylene-carbonate (VC) additives. These additives form a compliance coating on Si surface during cycling. Study the impact of the compliance polymer coating on the coulombic efficiency of Si materials.

RELEVANT USABC GOALS: PHEV-40: 144 Wh/l, 4000 deep-discharge cycles.

MILESTONES:

(a) Measure the adhesion of the triethyleneoxide (TEO)-containing conductive polymer binder, and characterize the electrode performance. (Mar. 13) **On schedule**

(b) Design and synthesize the alkyls-substituted VC additives. (Sep. 13) **On schedule**

(c) Investigate the performance of Si electrode using the substituted VC additive electrolyte *vs*. baseline electrolyte. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Both Si and Sn alloy with Li within the same voltage range, between 10 mV and 1 V. A comprehensive evaluation was performed of a composite electrode of Sn nanoparticles and a conductive polymer binder originally designed for Si. It was demonstrated that the electrode of Sn could cycle and provide a high gravimetric capacity (>500 mAh/g) with the polyfluorene-type conductive polymer[1] binder (PFM). The Sn primary particles were less than 150 nm wide and crystalline. The average diameter of Sn secondary particles was 270 nm, calculated based on the BET surface area. The composite electrodes contained a conductive polymer binder that made up 2 to 10 wt% of the laminate; no conductive constituents (*e.g.*, acetylene black) were added. The electrode that contained 5% conductive binder showed the best cycling performance, with a reversible capacity of 510 mAh/g (Fig. 1a). The crystallinity of Sn particles gradually degrades during cycling; pulverization of particles was observed after long-term cycling, resulting in capacity fade. The conductive polymer binder shows advantages over other conventional binders, such as poly(vinylidene fluoride) (PVDF) and carboxymethylcellulose (CMC) binders, because it provides electrical conductivity and strong adhesion during the volume expansion (Fig. 1b).

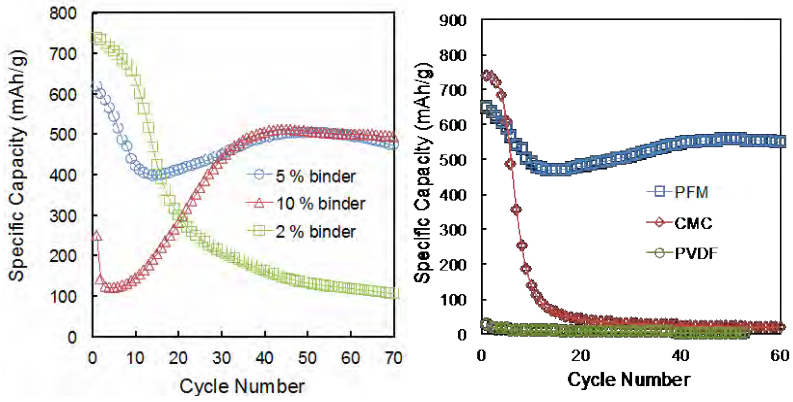


Figure 1. Pure Sn nanoparticle composite electrodes. (a) Different amount of PFM. (b) Different binders.

Collaborations: Collaborations are with BATT Program PIs, DOE national user facilities, and industrial partners. BATT collaborators include Vince Battaglia, Venkat Srinivasan, Phil Ross, and Xingcheng Xiao. DOE national user facility collaborators include Wanli Yang, ALS (LBNL); and Andy Minor, NCEM (LBNL). The industrial partner is General Motors.

Publications

1. J. Chong, *et al*. Surface stabilized $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials with high-rate capability and long cycle life for lithium ion batteries, *Nano Energy*, **2**, 283-293 (2013).
2. T. Xia, *et al*. Hydrogenated surface disorder enhances lithium-ion battery performance, to appear in *Nano Energy*.
3. S. Xun, *et al*. Conductive Polymer Binder-Enabled Cycling of Pure Tin Nanoparticle Composite Anode Electrodes for a Lithium-Ion Battery, to appear in *JES*.

[1] The conductive polymer is referred to Poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester), abbreviated as PFM.

Task 1.5-PI, INSTITUTION: Vincent Battaglia, Lawrence Berkeley National Laboratory

TASK TITLE: Electrode Architecture – Electrode fabrication and materials benchmarking

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Energy density of today's batteries is not high enough; cyclability is not high enough; calendar life is not long enough.

OBJECTIVE: To develop a robust set of processes for fabricating electrodes and to understand the fundamental properties that underlie electrode performance. Then to use the set of processes to evaluate small quantities of BATT Program developed materials.

GENERAL APPROACH: Materials are identified through our own testing or testing performed in the Applied Battery Research Program to make up a baseline chemistry. Ultimately a set of processes for each electrode is developed that is robust enough so that when a small quantity of comparable BATT Program material arrives, the same processes will result in an equally good electrode. The Program material is then evaluated in a series of rate and cycling tests and the results are compared to the baseline material. Sources of cell failure are identified and communicated back to the originator of the material. Materials that look promising are considered for further scale-up and testing or as a possible focus area.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. The group developed a fabrication manual over 5 years ago. The manual has been generally followed over the past two years. Many of the processes involved were developed based on a trial-and-error basis; although a methodical analysis of mixing order indicated that mixing the solids together before adding the polymer led to longer cycle life, and an analysis of carbon to polymer ratio indicated that this ratio should be kept between 1:5 and 4:5. It was recently determined that long mixing times can lead to a decline in viscosity.

EXPECTED STATUS SEP. 30, 2013: With regard to mixing, there are two steps: 1) mixing the solids together, 2) mixing the binder with the solids. By the end of the year the expectation is to know the most important of three variables: the first mixing-time, the first mixing speed, and the second mixing time. There is an expectation to understand to what extent the drop in viscosity with mixing is a good thing or a bad thing.

RELEVANT USABC GOALS: 200 to 300 Wh/kg; 1000 to 5000 full cycles; 10- to 15-year calendar life

MILESTONES:

(a) Measure the effect of mixing variables on electrode performance. (May 13) **On schedule**
(b) Measure the viscosity with mixing time and the effect on performance. (Jun. 13) **On schedule**
(c) Determine the optimum composition of an anode with high MW polymer. (Sep. 13) **On schedule**
(d) Test three materials developed in the BATT Program. (Sep. 13) **On schedule**

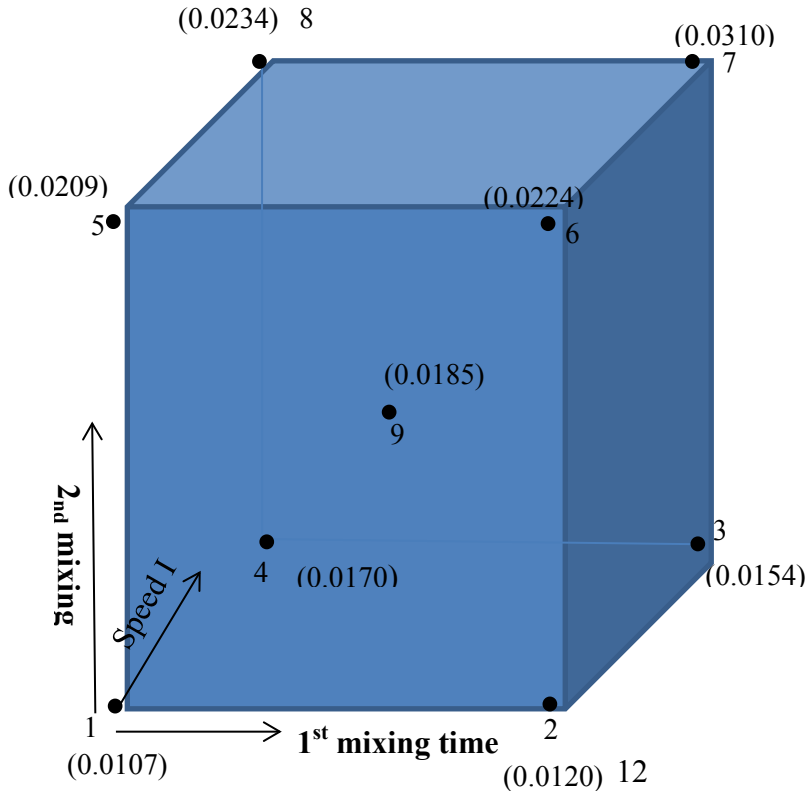
PROGRESS TOWARD MILESTONES

a.) Measure the effect of mixing variables on electrode performance. (May 13) **On schedule.**

Mixing of materials is a critical part of making a quality electrode. Our lab has investigated the fractional composition and mixing order of the components that make up an electrode. Part of this year's effort is the investigation of mixing time. In making an electrode, the active material and conductive carbon are combined with a high speed mixer in N-methylpyrrolidone (NMP). Once combined, the binder is added and the components are sheared together for a second mixing time. Our initial research of this overall process involves the investigation of the length of the first mixing time, the shear rate during the first mixing time, and the length of the second mixing time. The table below was followed in the development of 9 laminates.

Laminate	1st mixing(NMC9 4%wt+AB 2%wt)(min)	Speed I (krpm)	2nd mixing (PVDF 4%) (min)	Speed II (krpm)	Average conductivity (S cm^{-1})
1	4	2.5	10	2.5	0.0107
2	30	2.5	10	2.5	0.0120
3	30	10	10	2.5	0.0154
4	4	10	10	2.5	0.0170
5	4	2.5	120	2.5	0.0209
6	30	2.5	120	2.5	0.0224
7	30	10	120	2.5	0.0310
8	4	10	120	2.5	0.0234
9	17	5.5	65	2.5	0.0185

The results of conductivity measurements of cast laminates are provided in the last column and pictorially in the figure below.



These results indicate that the longest total mixing time combined with the highest shear rate results in the highest conductivity for the laminate. The data also indicate that the length of time of the second mixing step is most important of the three parameters.

Since conductivity of a laminate does not dictate cycle life or all factors of electrode performance, cells need to be made of these laminates and tested for rate capability, adhesion to the current collector, and cyclability.

These results should be reported in the next quarterly

BATT TASK 2

ANODES

Task 2.1-PI, INSTITUTION: Jack Vaughey, Argonne National Laboratory

TASK TITLE: Anodes ─ Novel Anode Materials

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy, poor low-temperature operation, and abuse tolerance limitations

OBJECTIVES: To overcome the electrochemical capacity limitations (both gravimetric and volumetric) of conventional carbon anodes by designing electrode architectures containing main group metal, metalloid or intermetallic components that can tolerate the volumetric expansion of the materials and provide an acceptable cycle life.

GENERAL APPROACH: To search for anode materials or formulations that provide an electrochemical potential a few hundred mV above the potential of metallic Li. Effort will be predominantly on Sn- and Si-based systems. A major thrust will be to design new electrode architectures in which an electrochemically active species is attached to the surface of a porous current collector providing a strong connection from the active species to the substrate. Such an approach minimizes the need for conductive additives and increases the power capabilities of these high energy anodes.

STATUS OCT. 1, 2012: Studies on the interfacial structure of Si-based electrodes bound to the substrate using metallic binders have been completed. Techniques have been determined and optimized to deposit electrochemically-active Si and Sn into porous substrates. Development of appropriate characterization tools to study active material/current collector interactions and their effect on cycle life and fade rate were optimized.

EXPECTED STATUS SEP. 30, 2013: A series of porous electrode structures with high loadings of active materials will be designed, created, and evaluated. Building on methodologies established earlier, diagnostic studies and *in situ* techniques will be employed to help refine required particle morphologies and other related issues associated with limited active material loadings and cycling.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

(a) Identify the thickness limits of Si film-based electrodes utilizing tools including tomography in a working electrode structure. (Mar. 13) **On schedule**

(b) Identify and demonstrate methodologies to incorporate higher levels. (>2 mAh/cm^2) of active Si into three-dimensional electrode structures. (Sep. 13) **On schedule**

(c) Demonstrate an *in situ* probe that can be used to correlate performance with sample preparation of an electrodeposited electrode. (Sep. 13) **On schedule**

(d) Synthesize, characterize, and evaluate the role of polymeric film coatings in increasing the cycle life of Si-based electrodes. (Sep 13) **On schedule**

PROGRESS TOWARD MILESTONES

Team: Lynn Trahey, Fulya Dogan, Xianghui Xiao, Fik Brushett (MIT)

This quarter, the team has been exploring the deposition of electrochemically active elements (elemental Si or Sn) into a foam structure and correlating the performance with the electrochemical and physical properties. Utilizing two different porous foam structures (discussed last quarter), the role of the deposition method on morphology and cycleability for Sn on a Cu three-dimensional electrode was investigated. Previous work had focused on electrodeposition to vary the morphology and it was concluded that the smoother films provide more stable cycling performance. This was attributed to a variety of factors including lower surface area and possibly less of the high reactivity crystal facets exposed to the electrolyte (Kostecki, *et al*., *Electrochem Comm*, 2011).

Synthetically, the films produced by an electrodeposition process can take some time depending on the quality of films desired. Upon review of the results, the use of electroless deposition was explored. As a process optimized industrially for Sn deposition, it is rapid and does not have 'line-of-sight' requirements. In Fig. 1, utilizing a commercial plating process, a Cu substrate was coated evenly with Sn. XRD analysis of the annealed samples at temperatures above 100°C indicated alloying to form Cu_xSn phases. Of particular note was the conformal nature of the deposition throughout the substrate, a trait identified earlier as beneficial to extended cycle life.

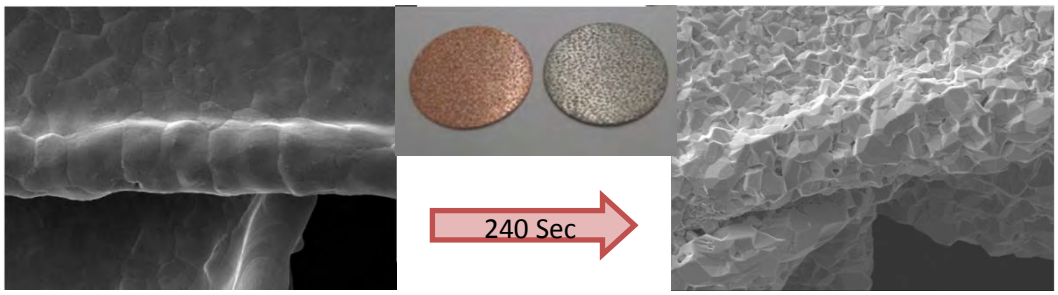


Figure 1. SEM images from the electroless deposition of metallic Sn from a commercial plating bath on a copper-foam. Total deposition time was 240 seconds.

Cycling of the films, Fig. 2, showed typical capacities and plateaus expected for a tin-based anode. More extended cycling is underway and will be reported.

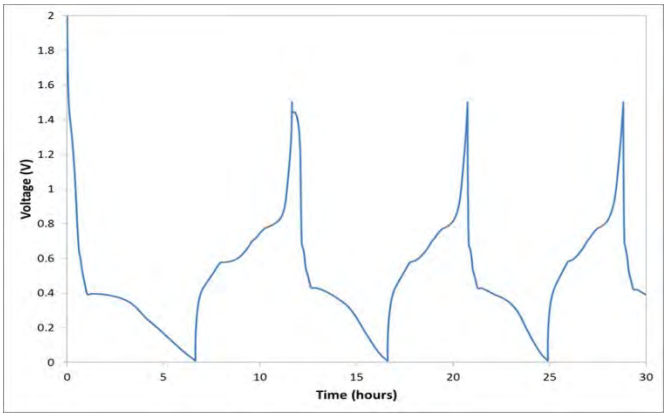


Figure 2. Cycling of electroless deposited Sn anode. Cell uses Gen2 electrolyte cycled in range of 0 to1.5 V at a C/5 rate.

TASK 2.2 - PI, INSTITUTION: Stanley Whittingham, Binghamton University

TASK TITLE - PROJECT: Anodes – Metal-based High Capacity Li-ion Anodes

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cost, safety and volumetric capacity limitations of lithium-ion batteries

OBJECTIVES: To replace the presently used carbon anodes with safer materials that have double the volumetric energy density, and will be compatible with low-cost layered oxide and phosphate cathodes and the associated electrolyte.

GENERAL APPROACH: Our anode approach is to synthesize, characterize and develop inexpensive materials that have a potential around 500 mV above that of pure Li (to minimize risk of Li plating and thus enhance safety), and to have higher volumetric energy densities than carbon. Emphasis will be placed on simple metal alloys/composites at the nano-size. Initially, Sn will be emphasized, building on what has been learned from our studies of the tin-cobalt anode, the only commercial anode besides carbon. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal, kinetic and structural stability to gain an understanding of their behavior.

STATUS OCT. 1, 2012: It has been shown that amorphous nano-size Sn alloys have a high capacity and maintain it on deep or shallow cycling, when stabilized with elements like Co. In contrast, bulk crystalline metals have a high capacity, but their capacity fades rapidly after several deep cycles in carbonate-based electrolytes due to resistive continuous SEI formation. A nano-Sn material which shows electrochemical behavior comparable to that of the Sn-Co alloy, but where all the Co has been replaced by low-cost Fe, has been successfully formed by mechanical synthesis. This material has a higher volumetric capacity than Conoco Philips CPG-8 Graphite and has been formed by two different synthesis methods.

EXPECTED STATUS SEP. 30, 2013: The proposed work will result in the development of durable metal-based Li-ion battery anodes with volumetric energy densities that approach double those of the state-of-the art carbons. The reaction mechanism of the nano-Sn materials and the role of the carbon in their electrochemical activity will be understood. The major cause of the first-cycle excess charge capacity will be determined, and approaches to mitigate it will be proposed. Some clues as to how to control the SEI on such materials to optimize lifetime will be obtained.

RELEVANT USABC GOALS: 5000 deep and 300,000 shallow discharge cycles, abuse tolerance to cell overcharge and short circuit, and maximum system volume.

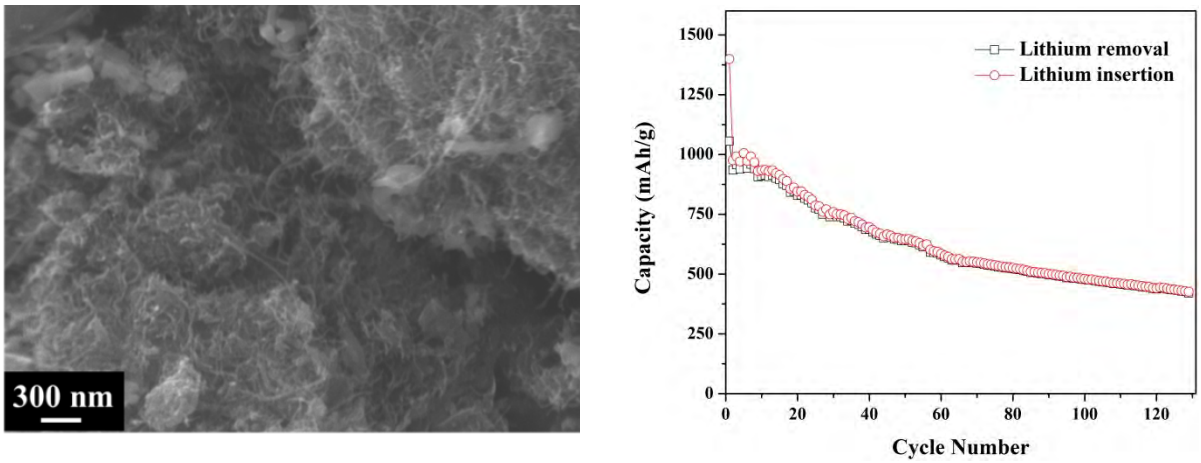
MILESTONES:

(a) Determine the reaction mechanism of the nano-Sn-Fe-C system. (May 13) **On schedule**
(b) Identify the cause of the first-cycle excess charge capacity; propose approaches to mitigate it. (Sep 13) **On schedule**
(c) Identify an anode candidate having an energy density of 2 Ah/cc for at least 100 cycles. (Sep. 13) **On schedule**
(d) Determine the electrochemistry of the leached nano-Si material, and compare to the standard Si. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The goal of this project is to synthesize new tin- and silicon-based anodes that have double the volumetric capacity of graphitic carbons and equivalent or better gravimetric capacity.

Milestones (c) and (d): In this quarter our work continued on nano-Si anode materials through a novel etching approach with a low-cost eutectic Al-Si alloy as the precursor. Earlier, the initial synthesis and electrochemical performance of this material was reported. An in-depth study of the structure using Rietveld refinement of the XRD data yielded a lattice parameter of a = 5.45(3) Å, V = 162.06 (6) $Å^3$, which is larger than for standard Si (a = 5.43Å, V = 160.15 $Å^3$), suggesting possibly a minor dissolution of other atoms in this nano-Si material. This observation is consistent with Energy Dispersive X-ray Spectroscopy (EDS) mapping, which showed that there is around 5 wt% Al uniformly distributed in the nano-Si particles. To further improve the electrochemical performance of this material, carbon nanotubes (CNT) were added to the active material because of their good electric conductivity and because they provide a ductile host matrix to buffer Si volume change. The SEM images (Fig. 1a) of the as-made material shows that the CNT were embedded into the nano-Si matrix with good dispersion. The cycling performance was found to be improved (Fig. 1b) by replacing half of the Si with CNT (graphite is also incorporated to avoid the dramatic capacity drop in the first cycle). The optimum composition of Si, CNT, and graphite obtained to date is 3:3:1.



(a) (b)

Figure 1. (a) SEM image and (b) electrochemical cycling of CNT+C incorporated nano-silicon anode material.

Further plans to meet or exceed milestones: None

Reason for changes from original milestones: None

Publication and Presentation:

1. W. Zhou, Z. Dong, H. Yang, F. Omenya, R. Zhang, N. A. Chernova and M. S. Whittingham, "Enhancing the Electrochemical Cycling of Si-carbon Anode with Electrolyte Additives for Lithium-ion Batteries," *Materials Research Society*, Boston, November 2012.
2. R. Zhang, W. Zhou, J., H. Zhou, Z. Dong, X. Hong and M. S. Whittingham, "Sn-Fe-C Composites as Anode Materials for Rechargeable Lithium-ion Batteries," *ibid*.

Task 2.3-PI, INSTITUTION: Prashant Kumta, University of Pittsburgh

TASK TITLE: Anodes – Nanoscale Heterostructures and Thermoplastic Resin Binders: Novel Li-ion Anode Systems

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF6+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low specific energy and energy density, poor cycle life and coulombic efficiency, large irreversible loss, poor rate capability, and calendar life.

OBJECTIVES: To identify new alternative nanostructured anode materials to replace graphite that will provide higher gravimetric and volumetric energy density. The goal is to replace carbon with an inexpensive nanostructured composite exhibiting higher capacity (1200 mAh/g) than carbon while exhibiting similar irreversible loss (<15%), coulombic efficiency (>99.9%), and cyclability. The project addresses the need to improve the capacity, specific energy, energy density, rate capability, cycle life, coulombic efficiency, and irreversible loss issues of Si anode.

GENERAL APPROACH: Our approach is to search for inexpensive silicon, carbon, and other inactive matrix-based composites (powders rather than thin films) that provide 1) an electrochemical potential a few hundred mV above the potential of Li, and 2) a capacity of 1200 mAh/g or greater (>2600 mAh/ml). The focus will be on exploring novel economical methods to generate nanoscale heterostructures of various Si nanostructures and different forms of C derived from graphitic carbon nanotubes (CNT) and new binders. Other electrochemically inactive matrices will also be explored. Promising electrodes will be tested in half cells against Li and compared to graphite as well as in full cells. Electrode structure, microstructure, rate capability, long- and short-term cyclability, coulombic efficiency, SEI origin and nature will also be studied.

STATUS OCT. 1, 2012: Nano-scale electrodes comprising Si-graphitic carbon-polymer derived C, and CNT related systems have been successfully synthesized and analyzed in half cells. The nano-composite Li-Si-C hetero-structures exhibit stable capacities of 700-3000 mAh/g with first cycle irreversible loss less than 15% and coulombic efficiency in the ~99.5-99.9% range.

EXPECTED STATUS SEP. 30, 2013: Efforts will continue to generate nano-composite 'core-shell', random, and aligned nanoscale Si, boron (B), and C exhibiting 1500 mAh/g and higher capacities. Research will be conducted to generate novel binders, explore novel synthesis and nano-scale microstructure affecting energy density, rate capability, first-cycle irreversible loss (FIR) and coulombic efficiency, characterize the SEI layer, and outline steps to yield stable capacity, reduce FIR, increase the coulombic efficiency and also improve the rate capability.

RELEVANT USABC GOALS: Available energy - CD Mode, 10 kW Rate: 3.4 kWh (10 mile) and 11.6 kWh (40 mile); Available Energy - CS Mode: 0.5 kWh (10 mile) and 0.3 kWh (40 mile); 10s peak pulse discharge power: 45 kW (10 mile) and 38 kW (40 mile); Peak Regen Pulse Power (10 sec): 30 kW (10 mile) and 25 kW (40 mile); Cold cranking power at -30^{o}C, 2sec-3 Pulses: 7kW; Calendar life: 15 years (at 40^{o}C); CS HEV Cycle Life, 50 Wh Profile: 300,000 Cycles

MILESTONES:

(a) Identify binders and approaches to reach stable reversible capacity $\geq$1500 mAh/g (Mar. 13) **On schedule**

(b) Identify strategies to achieve first cycle irreversible loss ($\leq$15%), efficiency ($\geq$99.95%), and rate capability matching carbon (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

In our previous report (Q-4, 2012) the development of silicon nanotube (SiNT) nanostructures as high-capacity and high-rate capability anodes for Li-ion batteries was reported. The first generation of SiNT were synthesized by CVD of Si on to a sacrificial inorganic matrix nanowire (IMNW) template. The morphology of the SiNTs depend largely on the morphology of the IMNWs. Thus, it is important to control the nano-scale morphological characteristics, such as nanowire agglomeration, wire smoothness, and aspect ratio, to name a few. In this quarter, variations in surfactant, pH, and long-chain polymer molecules were tested to improve the 1-D characteristics of the IMNWs. Use of ampiphilic long-chain molecules as a surfactant enhanced the dispersibility of the nanowires, increased the pH of the precursor solution to a more basic range (8.5<pH<10.5), and improved the smoothness of the nanowires. In another approach, synthesis of the IMNWs was conducted in an autoclave as the source of heat instead of using microwaves. This resulted in well-dispersed, smooth nanowires without the use of surfactants nor adjustments to the pH (Fig. 1).

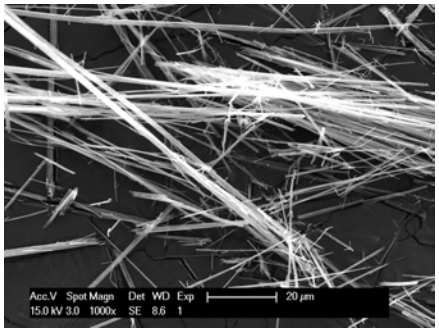


Figure 1. SEM image of smooth and unagglomerated inorganic matrix based nanowires generated in an autoclave.

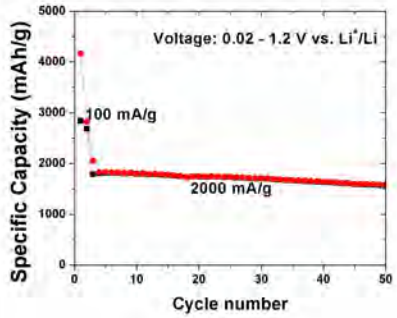


Figure 2. Variation of specific capacity *vs.* cycle number of SiNT cycled at different current densities.

The optimized IMNWs were dropcast on Cu foil current collector, then dried in an oven at 100°C to obtain a uniform coating of the nanowires on the foil. Subsequently, amorphous Si was sputtered for 1 h onto these nanowires with an RF power of 50 W. The Si-coated IMNWs were then dipped in a sacrificial solution to dissolve the nanowire template yielding hollow SiNTs. This binderless SiNT electrode was directly assembled in a 2016 coin cell and electrochemical characterization studies were conducted. The electrode exhibited a very high first-discharge capacity (~4100 mAh/g), with a first-cycle irreversible (FIR) loss of around 30%, which is attributed to the formation of SEI layer on the large, exposed surface area of the SiNTs (Fig. 3). The differential capacity plot provided in Fig. 3 shows a first cathodic peak at 0.25 V, identified as the lithiation of amorphous Si, followed by another peak at 0.1V which is due to the formation and amorphization of the Li_xSi alloys. At very high current rates (2 A/g), a capacity close to 1800 mAh/g was obtained. The excellent rate capability of the SiNT electrode was expected due to the decreased Li^+-ion diffusion distance in the hollow nanotubes. These smooth SiNTs also exhibit good cyclability with a capacity retention of 89% at the end of 50 cycles. Currently, efforts are on-going to decrease the FIR loss by generating an interface controlled electron conducting layer on the surface of the SiNTs.

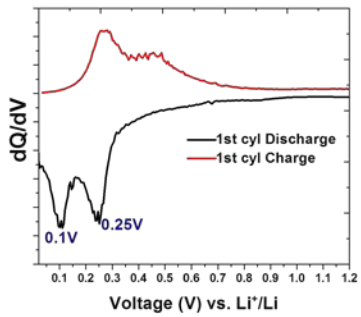


Figure 3. dQ/dV plot of the binder-less SiNT electrode cycled between 0.02 to 1.2 V *vs.* Li^+/Li at 100 mA/g.

TASK 2.4: PRINCIPAL INVESTIGATOR, INSTITUTION: Ji-Guang (Jason) Zhang and Jun Liu, Pacific Northwest National Laboratory

TASK TITLE – PROJECT: Anodes ─ Development of Silicon-based High Capacity Anodes

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, high cost, limited cycle life

OBJECTIVES: To develop high-capacity, low-cost electrodes with good cycle stability and rate capability to replace graphite in Li-ion batteries

GENERAL APPROACH: The main failure mechanism in Si-based anodes will be addressed using three approaches: improve the mechanical stability of Si-based anodes by manipulating the nano-structure of Si; improve electrical stability and conductivity of Si-based anodes by using conductive coating and binder; improve interface stability of Si-based anodes by choosing a stable electrolyte/binder with selective additives.

STATUS OCT. 1, 2012: Hollow core-shell structured porous Si-C nanocomposites with void space up to 30 nm between the Si core and the carbon shell have been designed and synthesized, and their electrochemical performance has been investigated. The porous core-shell structure of the Si-C composite helps to accommodate the large volume variations that occur during Li-insertion/extraction processes. In another effort, a conductive rigid skeleton-supported Si, such as B_4C/Si/C core-shell composite, was developed using the scalable ball-milling method. A high capacity of ~822 mAh/g (based on the full electrode) and capacity retention of ~94% over 100 cycles were obtained at a current density of ~0.63 A/g.

EXPECTED STATUS SEP. 30, 2013: The porous Si and the skeleton-supported core-shell structured composite (*e.g.,* B_4C/Si/C) will be further optimized. The optimized B_4C/Si/C material will be used as the baseline material for fundamental understanding of the failure mechanism. New binders, electrolyte, and electrolyte additives will be investigated to further improve the performance of Si-based anodes. New approaches will be developed to increase the capacity of thick Si-based anodes. An initial capacity of >800 mAh/g (based on the whole electrode) and ~80% capacity retention over 300 cycles will be obtained. Fundamental understanding of the formation and evolution of SEI layer, electrolyte additives, and the effect of electrode thickness will be investigated by *in situ* microscopic analysis.

RELEVANT USABC GOALS: >96 Wh/kg (for plug-in hybrid electric vehicles [PHEVs]), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

MILESTONES:

(a) Optimize the hollow core-shell structured porous Si and the rigid skeleton-supported Si composite for high capacity and stable cycling. (Mar. 13) **On schedule**

(b) Improve the performance of Si-based anodes with a capacity retention of >700 mAh/g over 250 cycles using new binders/electrolyte additives. (Sep. 13) **On schedule**

(c) Develop new approaches to improve the cyclability of thick electrodes (>3 mAh/cm^2). (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Si particles with pores of *ca*. 50 nm were developed for Li-ion anodes. The large pores are designed to accommodate the large volume change. This material demonstrated excellent cycling stability over hundreds of cycles with a capacity of *ca*. 600 mAh/g based on the entire laminate weight, which includes the binder and conductive carbon. Sodium carboxymethyl cellulose (CMC) binder and 1.0M $LiPF_6$ in EC/DMC (1:2 vol) electrolyte with 10% FEC additive were used in this investigation. Different Si loadings are being investigated to further improve the capacity. With a Si loading of *ca*. 40%, the electrode has a capacity of 570 mAh/g and no capacity fade after 400 cycles. When the Si loading is increased to 51%, it has a capacity of 620 mAh/g and more than 90% capacity retention over 300 cycles (Fig. 1).

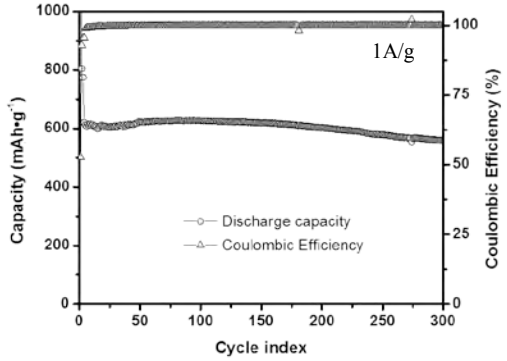


Figure 1. Cycling performance of the porous Si with ~51% Si in 1.0 M $LiPF_6$ in EC/DMC (1:2 vol) electrolyte with 10% FEC additive.

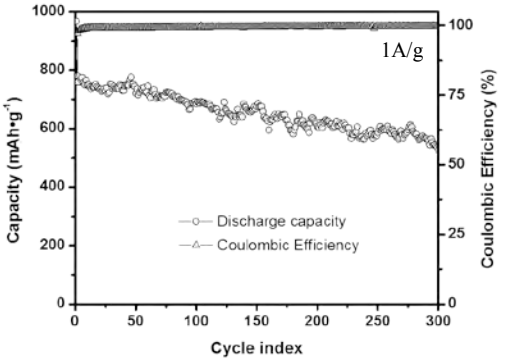


Figure 2. Cycling performance of the SBG433 in 1.0M $LiPF_6$ in EC/DMC (1:2 vol) electrolyte with 20% VC as additive.

In another effort, several different binders, including PVDF, CMC, sodium alginate, PEO, and CMC-SBR were investigated to further improve the cyclability and Coulombic efficiency of a B_4C-supported Si anode (Si:B_4C:graphite = 4:3:3). The samples using CMC binders demonstrated better stability than the other binders. Figure 2 shows the cycling performance of a SBG433 anode using CMC binder and 1.0 M $LiPF_6$ in EC/DMC (1:2 vol) electrolyte with 20% VC as additive. The sample retained 72% of its capacity after 300 cycles.

More work will is needed to reduce the first-cycle loss in porous Si samples. Further optimization of the porous Si and the B_4C-supported Si anode will be performed to improve their capacity and cycling stability. The electrode thickness, structure, porosity, binder, and electrolyte additives will be investigated. Fundamental understanding of capacity fading mechanisms, especially the structure of the SEI layer with electrolyte additives, will be part of the investigation.

Collaborations: Michael J. Sailor of UCSD (porous Si preparation).

Publications:

1. Wang CM, X Li, Z Wang, W Xu, J Liu, F Gao, L Kovarik, J Zhang, J Howe, DJ Burton, Z Liu, X Xiao, S Thevuthasan, and DR Baer. 2012. "In Situ TEM Investigation of Congruent Phase Transition and Structural Evolution of Nanostructured Silicon/Carbon Anode for Lithium Ion Batteries." *Nano Letters* 12(3):1624–1632. doi:10.1021/nl204559u.
2. Gu M, Y Li, X Li, SY Hu, X Zhang, W Xu, S Thevuthasan, DR Baer, J Zhang, J Liu, and CM Wang. 2012. "In-Situ TEM Study of Lithiation Behavior of Silicon Nanoparticles Attached to and Embedded in a Carbon Matrix." *ACS Nano* 6(9):8439-8447. doi:10.1021/nn303312m.

TASK 2.5 - PI, INSTITUTION: Chunmei Ban, National Renewable Energy Laboratory; Co-PIs Steven M. George and Se-Hee Lee, University of Colorado (CU), Boulder

TASK TITLE - PROJECT: Anodes – Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cost, low gravimetric and volumetric capacities, safety, rate capability, calendar and cycle life.

OBJECTIVES: To develop a low-cost, thick, and high-capacity Si anode with sustainable cycling performance. In FY13, our specific objectives are to develop a novel conductive and elastic scaffold by using Atomic Layer Deposition (ALD) and Molecular Layer Deposition (MLD), demonstrate the durable cycling by using our coating and electrode design, and investigate the effect of the atomic surface modification on the irreversible capacity loss.

GENERAL APPROACH: Chemical vapor deposition *via* silane decomposition on a hot filament has been used to synthesis the a-Si or nano-Si powders. Recently, a Nanocrystal RF Plasma Reactor was also utilized to synthesis Si/alloy nanocrystals with uniform size and shape. Size may be tuned from <10 to ~100 nm by varying the plasma conditions that will allow the study of how Si nanocrystal size affects the electrochemical performance. The conventional electrodes containing active material, conductive additive, and binder have been fabricated to evaluate the cycling properties. ALD is employed to coat both Si particles and Si electrodes in order to enhance the surface stability and electrode integrity.

STATUS OCT. 1, 2012: A Si anode coated with a unique copper/carbon composite was demonstrated to have a highly durable capacity at C/20 and C/10 with a coulombic efficiency of ~98%. ALD was employed on the thick Si anode to achieve the sustainable cycling performance. Recently, more durable cycling at higher rates (C/5 and C/3) has been achieved by using ALD-coated nano-Si anode. The thick Si electrodes (>15 μm) were recently sent to Dr. Vince Battaglia at LBNL for electrochemical testing.

EXPECTED STATUS SEP. 30, 2013: The optimal composition and structure of the ALD/MLD surface coatings will be established to improve the surface stability of Si particles as well as increase the integrity of Si electrodes. A thick Si anode with the appropriate ALD/MLD coatings will be demonstrated to have a high durable capacity as well as high rate capability. *In situ* characterization will be completed to better understand the structural evolution of the coated Si anodes during cycling.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES

(a) Identify and characterize the MLD hybrid metal-organic coating on Si anode. (Dec. 12) **Complete**
(b) Demonstrate durable cycling (>100 cycles) of the surface-engineered thick Si anodes (>15μm) at C/3. (Mar. 13) **On schedule**
(c) Characterize the effect of MLD metal alkoxide coatings on the cyclability of Si anodes, and demonstrate an MLD-coated Si anode with an irreversible capacity loss at 1st cycle less than 10%. (Jun. 13) **On schedule**
(d) Supply the optimized thick electrodes (>20um) fabricated in the MLD flexible network to LBNL for verification. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

To better accommodate the volume expansion of lithiated Si anodes, metal-organic hybrid films were grown on a Si anode using Molecular Layer Deposition (MLD). In this quarter, the growth of an aluminum alkoxide polymer (Alucone) is demonstrated using the sequential exposures of trimethylaluminum (TMA) and ethylene glycol (EG). Figure 1 depicts the self-limiting sequential reaction of Alucone MLD on a Si electrode. The Si electrodes were prepared with 60% Si nanoparticles (purchased from Aldrich without further treatment), 20% acetylene black, and 20% PVDF binder. The 10 nm Alucone films were coated on the as-prepared Si electrode by using MLD at 100 to 120°C. Field Emission Scanning Electron Microscopy (FESEM) was utilized to characterize the morphology of the Si electrodes before and after the MLD coating, as shown in Fig. 2. The images show that the original morphology was maintained after the 10 nm MLD Alucone coating. The Al was detected on the porous electrode using Dispersive X-ray spectroscopy (EDX), to confirm the presence of a conformal coating.

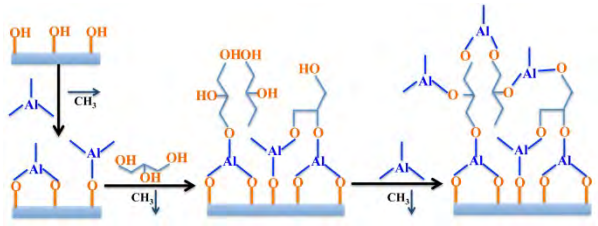


Figure 1. Schematic depicting Alucone MLD reaction.

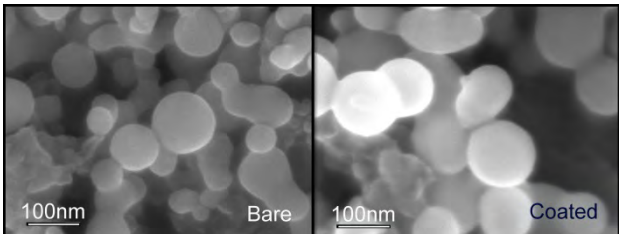


Figure 2. FESEM images of a bare and a coated Si electrode.

Electrochemical cycling performance of the Alucone-coated Si electrodes was investigated in a coin-cell configuration, with Li-metal as the counter electrode. All of the cells were first cycled at 175 mA/g (C/20) for 10 cycles, and then at 350 mA/g (C/10) in the voltage window between 0.05 and 1V. Figure 3 displays the significantly improved cycling stability of the Alucone MLD-coated Si electrode. The capacity obtained at a cycling rate of 0.1C is stabilized in the MLD-coated Si electrode. There is no major capacity fade observed up to 50 charge-discharge cycles, and the coulombic efficiency reaches *ca.* 100%. In contrast, the capacity of the bare Si anode decays to nearly zero after 28 charge-discharge cycles. Further characterization and analysis will be performed to understand the effect of the polymer coating on the Si alloy anode's cycleability.

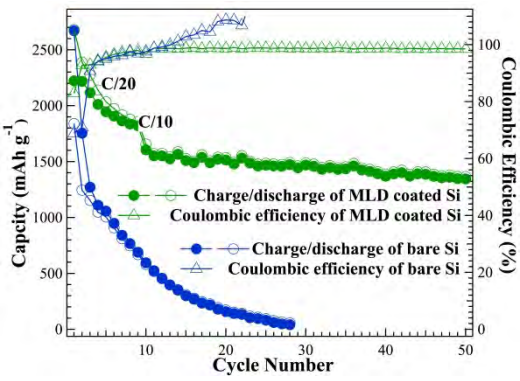


Figure 3. Comparison of bare Si and MLD-coated Si electrodes with regard to capacity and coulombic efficiency.

Presentation:

1. Atomic Layer Deposition of Al_2O_3 for Highly Improved Performance in Li-ion Battery Electrodes (Invited talk), 2012 Fall MRS, Boston, MA, USA.

TASK 2.6 - PI, INSTITUTION: Yury Gogotsi and Michel Barsoum, Drexel University

TASK TITLE - PROJECT: Anodes – New Layered Nanolaminates for Use in Lithium Battery Anodes

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Needs increased life, capacity and improved safety.

OBJECTIVES: Replace graphite with new solids: the layered binary carbides and nitrides known as MXenes, where the A-group element is selectively etched from the MAX phases – the latter ternary layered carbides and nitrides, may offer combined advantages of graphite and Si anodes with a higher capacity than graphite, less expansion, longer cycle life, and a lower cost than Si nanoparticles.

GENERAL APPROACH: Since, at this time the relationship between capacity and MXene phase chemistry is unknown, a rapid screening of as many MXene phases as possible is being carried out to determine the most promising chemistry by testing their performance in Li ion batteries. This work will also be guided by *ab initio* calculations.

STATUS OCT. 1, 2012: Fully exfoliated select MAX phases into two-dimensional layers of transition metal carbides or carbonitrides (MXenes) and tested the different MXenes as anode materials in LIBs.

EXPECTED STATUS SEP. 30, 2013: Complete a study of the effect of different exfoliated MXenes chemistries and structures on SEI formation. Optimize the performance of MXenes anode materials in LIBs, by selecting the best carbon and binder additives for the MXenes.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

(a) Select the best carbon additive and binder that results in the highest Li uptake for select MXenes. (Dec. 12) **Complete**

(b) Develop higher volumetric capacity anodes for LIBs than the commercial anodes. (Jun. 13) **On schedule**

(c) Produce MXenes of new chemistries (such as Nb_2C, V_2C) that can achieve anode capacities of 400 $mAhg^{-1}$ at cycling rates of 1C or faster. (Sep. 13) **On schedule**

(d) Produce MXene anodes with capability of delivering a stable performance at 10 C cycling rates. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Binder effect:

In our previous quarterly report, the effects of various carbon additives were investigated and it was found that onion-like carbon (OLC) had the most favorable effect on the Li uptake of the Ti_3C_2 anodes (240 mAh/g). Here the effect of different binders, PVDF, PEO, and alginate, on the performance of Ti_3C_2 anodes without carbon additives is reported. Figure 1 shows the specific capacity of Ti_3C_2 with different binders at a C/3 rate. Ti_3C_2 with 10 wt% alginate was found to be the best with a specific capacity greater than 150 mAh/g for more than 50 cycles. The increase in specific capacity is attributed to an increase in conductivity, as confirmed by EIS; the lowest R_{CT} (not shown) was obtained for a Ti_3C_2 electrode with 10 wt% alginate. Combining both alginate and OLC should result in the best performance, but it will be a challenge, as hydrophobic OLC does not readily disperse in alginate.

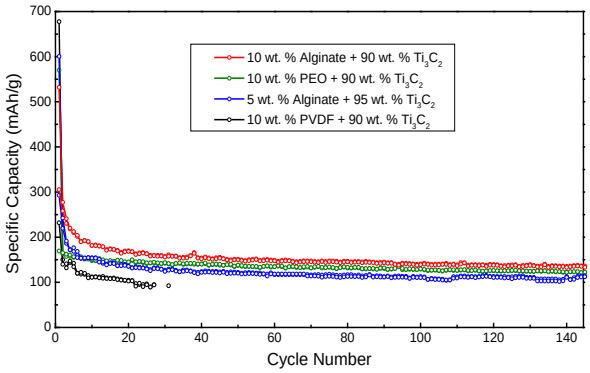


Figure 1. Effect of different binders on the capacity of stacked Ti_3C_2.

***In situ* Dilatometric Study:**

Figure 2 shows *in situ* dilatometry results for Ti_3C_2 (with 10 wt% PVDF and 10 wt% carbon black) during lithiation and delithiation. During the first lithiation cycle, the expansion in electrode thickness, $\Delta H_{Li}/H_o$, where H_o is the initial height of the electrode was around 7%. After around 20 cycles, $\Delta H_{Li}/H_o$ was <1%. The coulombic efficiency (orange curve in Fig. 2b) shows good agreement with the change in $\Delta H_{\text{delithiation}}/\Delta H_{lithiation}$ (Fig. 2a) (green curve in Fig. 2b). *Ex situ* XRD results after lithiation, however, showed a 21.5% increase in *c*-lattice parameter, $\Delta c_{Li}/c_o$, where c_o is the *c*-lattice parameter prior to lithiation. The difference between the c-lattice expansion and the 7% electrode expansion can be attributed to the fact that the electrode was porous thereby accommodating the expansion of the particles. Recall that expansion of the MXenes upon lithiation presumably only occurs along [0001].

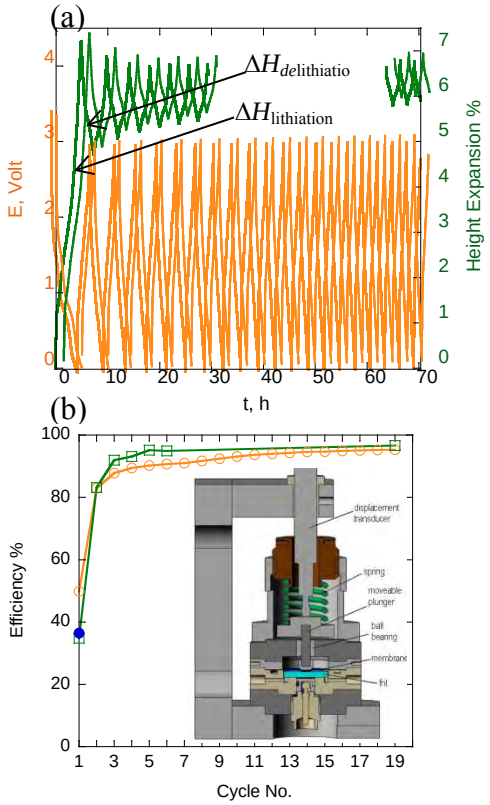


Figure 2. In-situ dilatometry results for stacked Ti_3C_2, (a) electrode thickness expansion %, and voltage during lithiation and delithiation, and (b) coulombic efficiency [orange] and $\Delta H_{\text{delithiation}}/\Delta H_{\text{lithiation}}$ *100 [green] vs. cycle number. The blue point is the % of change of lattice parameter $\Delta c_{\text{delithiation}}/\Delta c_{\text{lithiation}}$ *100. The inset is a schematic of the dilatometer.

Furthermore, when the irreversibility of the first cycle, as measured by $\Delta H_{\text{delithiation}}/\Delta H_{lithiation}$ (Fig. 2a), is compared to that estimated by comparing $\Delta c_{delithiation}/\Delta c_{Li}$ (blue solid circle in Fig.2b), excellent agreement is found. In other words, most of the 1st cycle irreversibility is due to Li trapped between the MXene layers. Work is ongoing to further understand the lithiation and delithiation mechanisms and to minimize the 1st cycle irreversibility, *e.g.*, by prelithiation.

Task 2.7-PI, INSTITUTION: Donghai Wang and Michael Hickner, Pennsylvania State University

TASK TITLE - PROJECT: Anodes: Synthesis and Characterization of Structured Si/SiO_x-based Nanocomposite Anodes and Functional Polymer Binders

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy, poor capacity cycling, large initial irreversible capacity.

OBJECTIVES: Obtain high-performance Si anode materials by developing novel-structured Si/SiO_x-carbon nanocomposites and polymer binders to improve electrode kinetics and cycling life, and decrease initial irreversible capacity loss.

GENERAL APPROACH: Our approach is to synthesize Si/SiO_x-carbon nanocomposites with controlled nanostructures to improve kinetics and cycling stability upon lithiation/delithiation. New polymer binders will be developed with controlled mechanical properties by variation in crosslinking and SiO_x or carbon surface-binding functionality. These new binders are meant to help stabilize Si particles by providing a low-swelling polymer matrix with strong interactions with the anode particles and low electrolyte uptake.

STATUS OCT. 1, 2012: Silicon-carbon nanocomposites were developed with capacity above 800 mAh/g and capacity retention of 75% after 100 cycles. Evaluation of Si/SiO_x nanoparticles with stable capacity of 650 mAh/g after 500 cycles has been completed. New materials strategies for low electrolyte uptake sulfonated binders with variable crosslinking are reported with their performance evaluated against CMC-SBR and Na-CMC controls. Capacity degradation is still observed within 50 cycles and new binder formulations are being developed.

EXPECTED STATUS SEP. 30, 2013: Synthesis, characterization and electrochemical performance evaluation of Si/SiO_x-carbon nanocomposites will be completed to demonstrate optimized electrodes with stable cycle life and increased efficiency. Increased polymer binder performance with carboxylate-containing, cross-linked, mechanically stiff polymers will be demonstrated. Structure-property relationships for creating new, non-conductive binders that are soluble in benign solvents will be reported.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

(a) Synthesize and characterize three types of Si/SiO_x-carbon nanocomposites. (Jan. 13) **On schedule**
(b) Demonstrate new crosslinking chemistry involving sulfonates, carboxylates, and azide chemistries for low-swelling polymer binders. (Jan. 13) **On schedule**
(c) Identify at least one Si/SiOx-carbon nanocomposite anode with a reversible specific capacity of at least 1000 mAh/g over 200 cycles. (May 13) **On schedule**
(d) Identify and optimize at least one polymer binder and processing solvent that shows better cycling performance than the reported binders with commercial Si nanoparticles. (May 13) **On schedule**
(e) Supply laminates of the optimized electrodes with electrode capacity of 800 mAh/g that cycle 100 cycles to BATT PIs. (Aug. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Si-based anode materials:

A novel micron-sized Si-C composite composed of interconnected nano-scale building blocks of Si and carbon was synthesized *via* a scalable and low-cost method. The composite was also thoroughly characterized by a variety of physical characterization methods including XRD, XPS, FT-IR, Raman, TEM, and SEM. The SEM image shows that the average particle size of the composite is around 20 μm (Fig. 1A). The Si-C composite exhibits a reversible capacity of 1.459 Ah/g after 200 cycles at 1 A/g with capacity retention of 97.8% (Fig. 1B) and a tap density of 0.78 g/cm^3. The first-cycle coulombic efficiency is 77%. Capacities of 1100 and 700 mAh/g can be obtained at the high current densities of 6.4 and 12.8 A/g, respectively (Fig. 1C). The performance is attributed to the nanoscale size of the primary particles, the interconnected carbon, and the Si networks that maintain internal electrical contact. Further investigations on primary unit size and the effects of carbon coatings are ongoing.

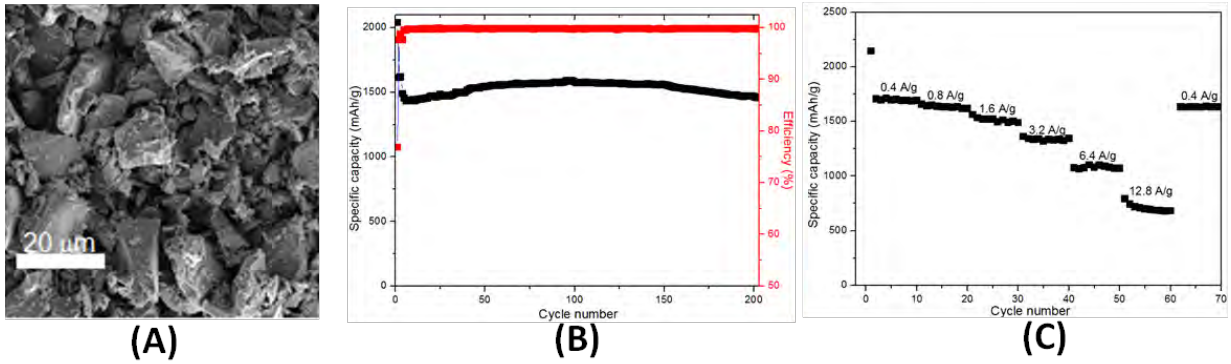


Figure 1. (A) SEM image of the micro-sized Si-C composite. (B) Cycling performance of the Si-C composite in 200 cycles between 0.01-1.5V. (C) Rate performance of the Si-C composite.

Polymer binders:

Sulfonated poly(ether ether ketone) (SPEEK) binders have shown better rate capability than NaCMC binder materials in Si-based anodes fabricated from commercial Si nanoparticles. Analysis of the performance of SPEEK binders under long-term cycle testing and rate testing continues. Figure 2 (left) shows the capacity *vs*. cycle number data (400 mA/g) for 100 cycles for a commercial Si-nanoparticle-SPEEK anode when cycled against Li metal. The mass loading of the electrode was about 1.5 mg/cm^2. FEC was added to the electrolyte to assist in maintaining capacity with cycling. The rate capability of this electrode is shown in Fig. 2 (right). It is believed that the SPEEK binder either is promoting ion conductivity in the electrode or impacting the surface of the Si nanoparticles. The mechanisms of this binder are currently being explored.

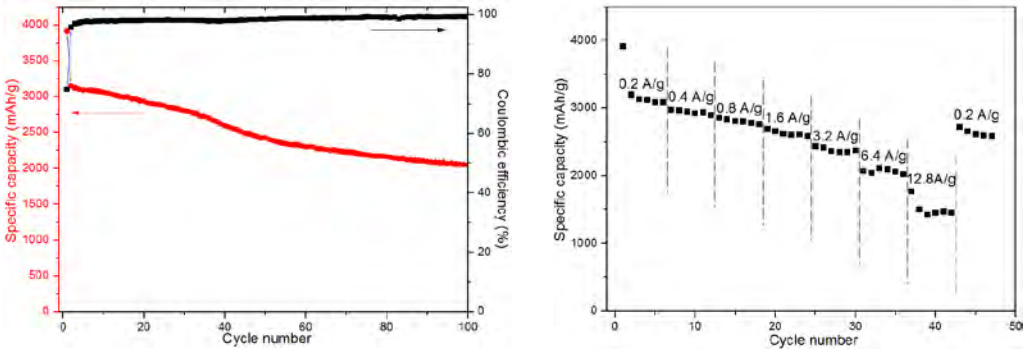


Figure 2. (left) Long-term cycling capacity and coulombic efficiency at 400 mA/g and (right) rate capability of commercial Si-nanoparticle-SPEEK binder-based anodes in half cells.

TASK 2.8 - PI, INSTITUTION: Yi Cui, Stanford University

TASK TITLE - PROJECT: Anodes – Wiring up Silicon Nanoparticles for High Performance Lithium-ion Battery Anodes

BASELINE SYSTEMS: Conoco Phillips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, low efficiency, short cycle life, and safety issues

OBJECTIVES: Overcome the charge capacity limitations of conventional carbon anodes by designing optimized nano-architectured silicon electrodes as follows: 1) fabricate novel nanostructures that show improved cycle life, and 2) develop methods to study the lithiation/delithiation process to understand volume expansion for higher efficiency.

GENERAL APPROACH: This project explores 1) new types of nanostructured anodes, 2) methods for controlling SEI growth and electrode stability, and 3) the nature of volume changes in Si nanostructures. Over the course of the year, a variety of nanostructured electrodes will be developed, with particular emphasis placed on developing structures based on conductive frameworks and also making high performance electrodes with both nano- and micron-sized Si particles. In addition, hollow/porous nanostructures will be developed and optimized for SEI control in these electrode structures. Finally, separate efforts will be dedicated to understanding the fundamentals of volume expansion in Si nanostructures through *in situ* and *ex situ* single nanostructure observation; specifically, the fracture properties of Si with different crystallinity will be studied. This project was initiated January 1, 2011.

STATUS OCT. 1, 2012: A variety of conductive secondary additives (polymer, hydrogel, etc.) were developed. Nano- and micron-sized Si particle electrodes were fabricated with these additives. A variety of spherical, tubular, and porous Si nanostructures were fabricated and incorporated into Si anode architectures. Suitable amorphous and crystalline Si nanostructures with controlled sizes have been developed for study.

EXPECTED STATUS SEP. 30, 2013: Electrodes with cycle life >1000 cycles in a half cell and CE >99.5% will have been demonstrated from nano- and micron-sized Si particles. The critical size for fracture of amorphous nanostructures will have been found.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

(a) Develop conductive polymer additive/binder, incorporate into electrodes. (Jan 13) **On schedule**
(b) Determine the effect of electrode additives, coatings, and porosity on SEI thickness and properties. (Apr. 13) **On schedule**
(c) Optimize nano/micro particle electrodes for high capacity, >1000 cycles, >99.7% CE. (Jul. 13) **On schedule**
(d) Use *in situ* TEM and *ex situ* SEM to test critical size and rate for fracture for crystalline, polycrystalline, and amorphous Si nanostructures. (Jul. 13) **Complete**

PROGRESS TOWARD MILESTONES

Unexpected two-phase lithiation in amorphous Si. *In situ* TEM experiments investigating the lithiation of crystalline Si nanoparticles were reported previously. Interesting kinetic behavior was uncovered in which the reaction process slowed drastically as lithiation proceeded. Crystalline Si is commonly used as the active material in nanostructured Si anodes, but it is equally important to study reaction processes in amorphous Si, since this material is also used quite often. In addition, crystalline Si is converted to amorphous Si after the first cycle.

For these experiments, amorphous hydrogenated Si spheres were fabricated *via* decomposition of trisilane in supercritical n-hexane at high temperature. The *in situ* tests were performed with a specialized TEM holder (Nanofactory Instruments, AB) in which two probes can be spatially manipulated while an electrical bias is applied. A nanoscale electrochemical cell is fabricated on the holder, with the amorphous Si spheres as the working electrode, Li metal as the counter electrode, and a Li_2O layer as the solid electrolyte (Fig. 1a) [1]. When a negative bias was applied to the amorphous Si electrode, Li diffused into the Si and it became lithiated, as shown in Fig. 1b-e.

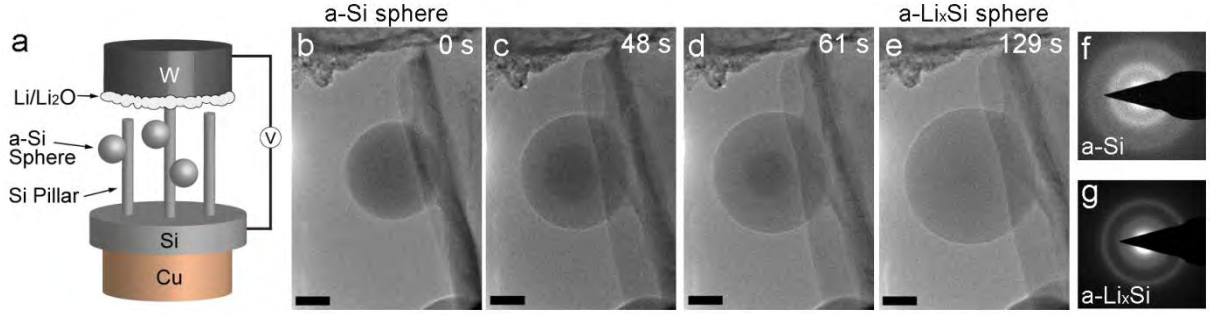


Figure 1. (a) Schematic of in-situ device. (b-e) Time series of amorphous Si sphere during lithiation. (f, g) Electron diffraction patterns before and after lithiation.

The sharp contrast between the core and shell regions in Fig. 1c, d during lithiation is unexpected because this indicates that there is a reaction front that sweeps through the particle. The lithiation mechanism is important to understand because it affects fracture behavior and reaction kinetics. Analysis of the TEM images found that this contrast difference could not be caused by conventional diffusion. Previously, it was thought that amorphous Si is lithiated *via* a single-phase reaction because of its sloping potential profile in electrochemical experiments, but these TEM experiments show that it is a two-phase reaction. Further experiments showed that this two-phase behavior was limited to the first lithiation – later lithiation cycles did not show a reaction front. The two-phase reaction is attributed to the activation energy required to break up the Si-Si bonds in the amorphous Si phase, which is actually similar to crystalline Si lithiation. The single-phase reaction on later cycles may occur because of lingering damage (dangling bonds) in the amorphous Si or perhaps even trapped Li in the structure.

Overall, this study shows that the first lithiation of amorphous and crystalline Si is more similar than previously thought. However, there are some important differences: 1) amorphous Si particles, up to 800 nm in diameter, do not fracture upon lithiation, whereas crystalline Si particles $\gtrsim$200 nm do fracture, and 2) the amorphous Si particles show better kinetics (there is no reaction front slowing, as in crystalline Si). These features suggest that amorphous Si may be more advantageous in real Si electrodes.

TASK 2.9 - PI, INSTITUTION: Kwai Chan and Michael Miller, Southwest Research Institute

TASK TITLE - PROJECT: Anodes – Synthesis and Characterization of Silicon Clathrates for Anode Applications in Lithium-ion Batteries

BASELINE SYSTEMS: Conoco Phillips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low-energy density, low-power density, and short calendar and cycle lives

OBJECTIVES: The objectives are to synthesize and characterize silicon clathrate anodes designed to exhibit small volume expansion during lithiation, high specific energy density, while avoiding capacity fading and improving battery life and abuse tolerance.

GENERAL APPROACH: Our approach is to synthesize guest-free Type I silicon clathrate (Si_{46}, space group $Pm\bar{3}n$) using high-pressure and high-temperature experimental methods, including a newly-developed arc-melt technique. Concurrently, an investigational route for direct synthesis of guest-free clathrate is being explored, and *ab initio* and classical molecular dynamics (MD) computations will be performed to identify lithiation pathways. The silicon clathrates will be utilized to fabricate prototype silicon clathrate anodes. Electrochemical characterization will be performed to evaluate and improve, if necessary, anode performance including cyclic stability. The final year of the program will be directed at the design, assembly, and characterization of a complete (anode/cathode) small-scale, prototype battery suitable for concept demonstration.

STATUS OCT. 1, 2012: Possible reaction pathways for the formation of Si_{46}**,** Li_xSi_{46}, $Li_{15}Si_4$, and $Li_xM_ySi_{46-y}$l have been identified using first-principles methods. Several hundred grams of Type I silicon clathrates and metal-silicon clathrate alloys have been fabricated by two different processing methods (arc-melting and direct solution-synthesis) and have been characterized for purity. Several half-cells of Si anodes have been constructed and characterized for electrochemical properties.

EXPECTED STATUS SEP. 30, 2013: Several half-cells of silicon clathrate anodes will have been fabricated using Year 2 materials, in combination with best-case additives and electrolyte formulations. The electrochemical properties of prototype anodes will have been characterized using a half-cell test apparatus. A suite of techniques will have been utilized to obtain a comprehensive understanding of the electrochemical behavior of such anodes under cyclic Li^+ intercalation/de-intercalation conditions. An extensive post-mortem evaluation will be carried out to assess the structural and mechanical state of anode materials, and the experimental results will be compared against corresponding first-principles computations.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

(a) Construct and evaluate several electrochemical half cells using anode materials synthesized in Year 2, combined with best-case additives and electrolyte formulations. (Jan. 13) **On schedule**

(b) Characterize electrochemical properties of silicon clathrate anodes made from Year 2 materials. (Apr. 13) **On schedule**

(c) Identify structural and mechanical states of silicon clathrate anodes during lithiation and delithiation processes and validate against theoretical calculations. (Jul. 13) **On schedule**

(d) Achieve a reversible capacity of 400 mAh/g after 50 cycles at C/15 for either Si_{46} or $A_8M_ySi_{46-y}$ (A = Ba, Na; M = Al, Cu). (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Task 1 – Synthesis of Type I Silicon Clathrates

Synthetic work during this quarter was directed at the development of process techniques for preparing the Zintl phase of sodium silicide (NaSi) starting from impure, fuel grade $NaSi_{1.5}$. The Zintl phase is a reactive precursor needed to undertake a low-temperature solution-based pathway reported earlier for the synthesis of empty silicon clathrate (Si_{46}). Using sealed vessels in an inert furnace, the transition of $NaSi_{1.4}$ to the Zintl phase was performed at high temperature and pressure in the presence of excess NaH over 48 hrs. XRD analysis of the product (Fig. 1) provided evidence for the transformation. Additional trials for the solution synthesis of Si_{46} using the Zintl phase are planned for next quarter.

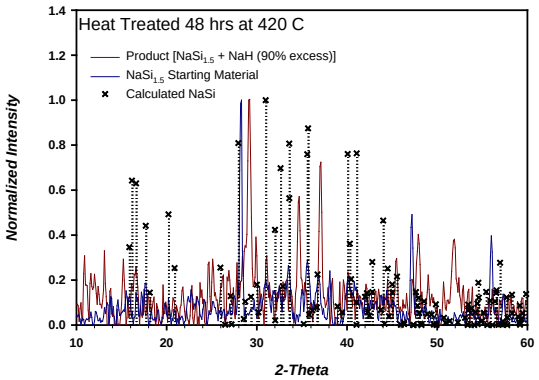


Figure 1. Powder XRD patterns for starting material and reaction product showing shifts in key reflections attributed to the formation of the Zintl phase of NaSi.

Task 2 – Molecular Modeling of Silicon Clathrates

Efforts to identify potential lithiation pathways for Na-stabilized Si_{46} continued in this quarter and the results were evaluated against those of Ba-stabilized and empty Si_{46} clathrates by comparing the energy of formation and the volume change as a function of the number of Li atoms.

Task 3 – Prototype Silicon Clathrate Anode Fabrication

The framework-substituted Type I clathrate alloy, $Ba_8Al_8Si_{38}$, synthesized in bulk (200 g) during the previous quarter was carefully processed *via* ball milling and sequential particle sizing to enable the preparation and testing of prototype anodes. The process yielded sub-micron particles (Fig. 2) without compromising crystallographic purity. The milled clathrate material was then combined with binder and additive to form a slurry that was easily cast into thin-film anodes for electrochemical evaluation.

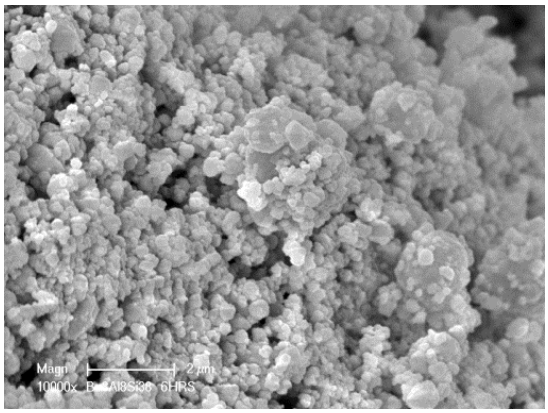


Figure 2. Particle morphology of processed $Ba_8Al_8Si_{38}$ milled powder for prototype anodes.

Task 4 – Half-Cell Electrochemical Characterization

Electrochemical cycling measurements were made on a prototype anode of the $Ba_8Al_8Si_{38}$ prepared in Task 3. Significant improvements in the time required to attain a stable OCP (2.7 V) and in the intercalation kinetics of the cell during discharge were observed from the processed, sub-micron anode material. Notably, a 10-fold increase in the C-rate was achievable while surpassing the theoretical capacity (259 mA·h/g) of the anode (Fig. 3). However, further improvements are needed to reduce the first-cycle capacity loss while maintaining similarly-high C-rates during the charging cycles (de-intercalation).

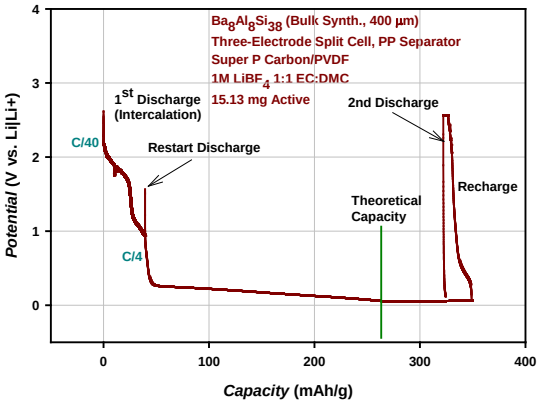


Figure 3. Electrochemical intercalation of Li^+ into prototype anode from processed $Ba_8Al_8Si_{38}$.

BATT TASK 3

ELECTROLYTES

TASK 3.1 - PI, INSTITUTION: John Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes – Interfacial and Bulk Properties and Stability

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Poor cycle and calendar life, low power and energy densities, particularly at low temperatures (-30°C).

OBJECTIVES:
1. Determine the role of electrolyte structure upon bulk transport and intrinsic electrochemical kinetics and how it contributes to cell impedance (Energy/ power density).
2. Determine chemical and electrochemical stability of electrolyte materials to allow elucidation of the structure of and the design of passivating layers (*e.g.*, SEI).

GENERAL APPROACH: A physical organic chemistry approach is taken to electrolyte design, where the molecular structure is varied to provide insight into the processes that may affect the performance of the battery. This involves model compounds as well as synthesis of new materials to test hypotheses which may explain battery behavior.

STATUS, OCT. 1, 2012: Carbon nanotubes and other carbonaceous conducting elements have been further modified with a broader range of chemical groups (PEGs, imide and malonato-difluoroborate anions) and the effects on composite electrode performance determined. Combination of these modifications with variations of binder polymers were studied to determine how electrode ink formulation affects the electrode morphology and electrode performance, particularly for thick, high energy electrodes.

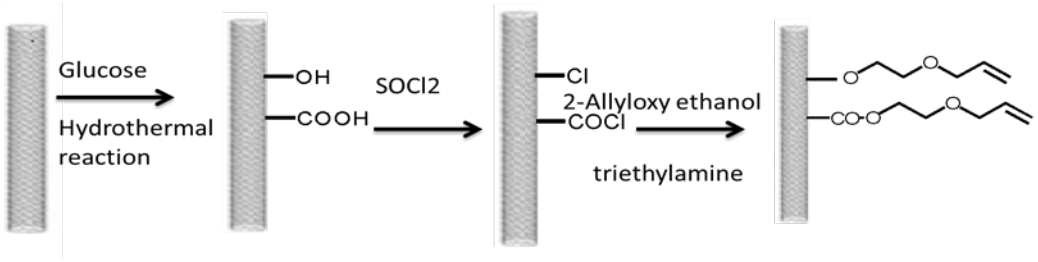
EXPECTED STATUS, SEP. 30, 2013: The demonstration of the advantages and drawbacks of single-ion conductor materials will be complete. The exploration of surface functionalization of conducting additives and the effect of interfacial impedance will be complete. Measurement of the composite electrode thickness increases made possible by use of single-ion conductor electrolytes will provide data to estimate the potential energy and power density increases. Initial estimates of calendar and cycle life will be complete. A completely solid state battery will be constructed with no solvent.

RELEVANT USABC GOALS: *Available energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10 s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile); *Cycle life*: 5000 cycles (10 mile) and 3000 cycles (40 mile); *Calendar life*: 15 years (at 40°C); cold cranking capability to -30°C; abuse tolerance.

MILESTONES:
(a) Complete construction and test of three different thicknesses of composite cathode electrode cells using gel electrolyte. (Apr. 13) **On schedule**
(b) Construct and test single-ion conductor solid-state cells with no free solvents and composite anodes and cathodes. (Sep. 12) **On schedule**

PROGRESS TOWARD MILESTONES

1) Surface modification of conducting carbon components in composite electrodes.
Modification of carbon surfaces have been achieved that are suitable for functionalization with imide anions:



The carbon nanotubes are functionalized by the hydrothermal reaction of glucose followed by chlorination and reaction with the allyl function which is used to attach the anion function. The course of the reaction is followed by TGA analysis of the carbons after each reaction step that shows the increasing weight of organic groups on the surface as measured by the weight loss. FTIR of the carbons is also used to monitor the functionalization.

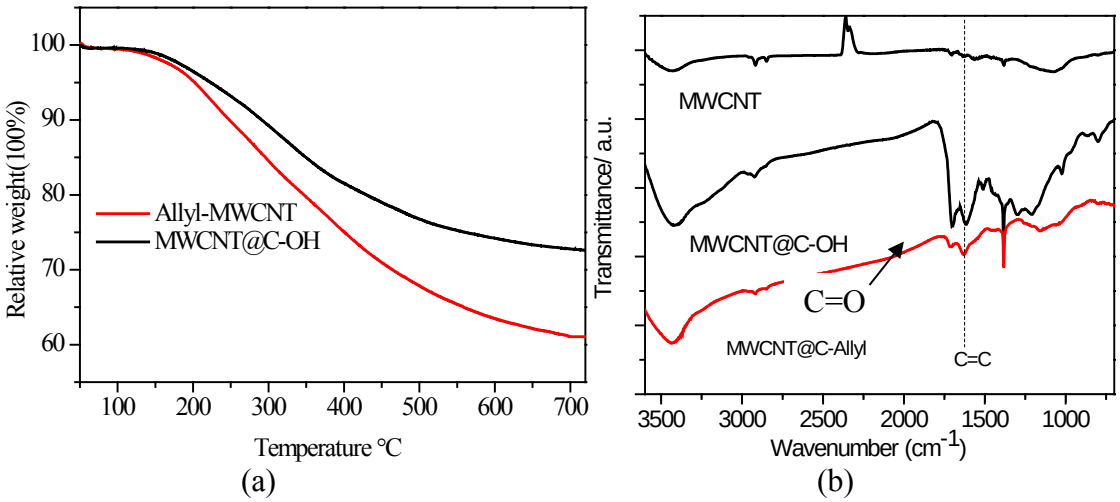
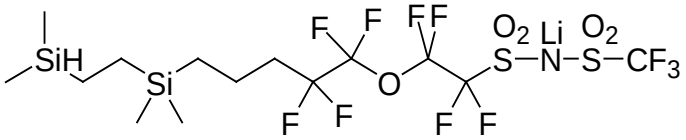


Figure 1. (a) TGA curves of the as-prepared Allyl- MWCNT and pristine MWCNT; (b) IR spectra of the as-prepared MWCNT@C-OH and pristine MWCNT and allyl-MWCNT.

The allyl group on the carbon will be functionalized with the imide group:



This material has been successfully prepared on a larger scale (10g) and will be used to functionalize the carbons as well as the polymers used as separators and binders.

2) Use of single-ion conductor polyelectrolytes (gel and dry polymer) to provide high energy composite electrodes due to increased thickness.
The successful preparation of the functionalized carbon combined with preparation of larger amounts of polymer single-ion conductors will facilitate this activity in the coming quarters.

TASK 3.2 - PI, INSTITUTION: Khalil Amine and Larry Curtiss, Argonne National Laboratory

TASK TITLE - PROJECT: Electrolytes ─ Advanced Electrolyte and Electrolyte Additives

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cycle/calendar life, abuse tolerance

OBJECTIVES: Develop advanced quantum chemical models to predict functional additives that form stable SEI on carbon anodes and cathodes and redox shuttles for overcharge protection. Synthesize suitable additives predicted by model, characterize, and perform extensive cycle and calendar life tests.

GENERAL APPROACH: Search for new electrolytic additives that react in a preferential manner to prevent detrimental decomposition of other cell components using experiment and theory. Use quantum chemical screening to predict oxidation and reduction potentials and decomposition pathways that form desirable coatings and prevent overcharge. Investigate SEI formation using a combination of computational and experimental techniques.

STATUS OCT. 1, 2012: Exploration of full decomposition pathways for selected additive candidates were carried out using advanced quantum chemical techniques. Experimental testing and characterization of the additives have been performed. Quantum chemical studies of the reaction energies for decomposition of shuttle candidates and experimental testing were carried out..

EXPECTED STATUS SEP. 30, 2013: Screening of redox shuttles based on tri- and quarter-phenyls with various functional groups using advanced quantum chemical calculations of redox potentials, exploration of full decomposition pathways, and surface interactions. Experimental testing and characterization of the selected shuttles will be performed. Computational and experimental investigations of the SEI structure and properties from oxalate based additives.

RELEVANT USABC GOALS: 10-s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile.)

MILESTONES:

(a) Screening of redox potentials and oxidative stabilities of derivatived ter- and quaterphenyls R-$C_6H_4(C_6H_4)_mC_6H_4$-R (m=1,2), each with twelve different functional groups R, for use as redox shuttles for overcharge protection using advanced computational techniques. (Jan. 13) **On schedule**

(b) Synthesis of at least one ter- and quarterphenyl based shuttle from theoretical predictions. (Apr. 13) **On schedule**

(c) Characterization of synthesized redox shuttles from experiment and computational studies of spectroscopic properties. (Jun. 13) **On schedule**

(d) Demonstration of overcharge protection and cell balancing properties of selected redox candidates. (Sep 13) **On schedule**

(e) Completion of modeling and characterization of polymeric SEI formed from an oxalate based additive on an anode surface. (Sep 13) **On schedule**

PROGRESS TOWARD MILESTONES

Our approach for the development of additives for SEI and redox shuttles for overcharge protection involves screening of reduction and oxidation potentials through the use of accurate density functional methods followed by an investigation of the mechanism of decomposition through investigation of reaction pathways. Finally the theoretical results are related to the performance of the additives in a battery cell. A good SEI prevents further electrolysis of the electrolyte and increases battery cycle life.

Density functional methods were used to examine one and two electron reduction reactions of the maleic, citraconic, and dimethylmaleic anhydrides shown in Fig. 1. The calculated reduction potentials are all greater than 2 V *vs.* Li/Li^+ due to conjugation, but decrease as more electron releasing methyl groups are attached. There are various reaction pathways for decomposition after reduction including anionic polymerization following one electron reduction, formation of Li_2CO_3 after two electron reduction, and reaction with ethylene carbonate (EC) after one electron reduction. The first pathway (polymerization) has been examined in detail and was found favorable.

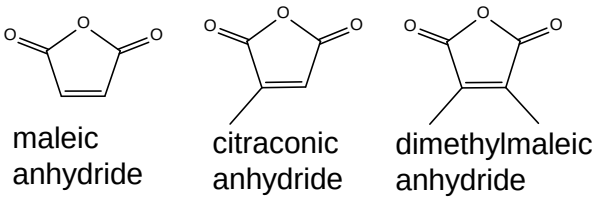


Figure 1. Structures of the three anhydrides.

Anionic polymerization can take place after two anion radicals bond to form a dianion dimer which then polymerizes by reacting with other species at both ends. All dimerization processes for the three anydrides are exothermic with the maleic anhydride dianion dimer being the most stable of the three (-3.73 eV with respect to starting materials) followed by citraconic (-2.97) and dimethylmaleic (-2.18). The ordering is due to hyperconjugation and steric effects associated with the methyl groups. Further reaction with EC of the dianion dimers at an ethylene carbon is possible. The resulting maleic anhydride dianion dimer EC species is the most stable of the three (-4.50 eV), followed by citraconic (-3.61), and dimethylmaleic (-2.45). Addition of a third EC increases the free energy in all three systems by about half an eV, limiting polymer growth. Based on the favorable exothermicities of this general reaction pathway these should be potential additives for SEI formation.

Experimentally, the performance of citraconic anhydride exhibited excellent performance. The citraconic anhydride additive (1%) was added to the electrolyte of a cell having the following components: $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$//1.2M $LiPF_6$ EC/EMC//MCMB. It was found that the citraconic anhydride is easily reduced, consistent with the theoretical predictions. It also results in improved cycling performance compared to the electrolyte without the additive as shown in Fig. 2.

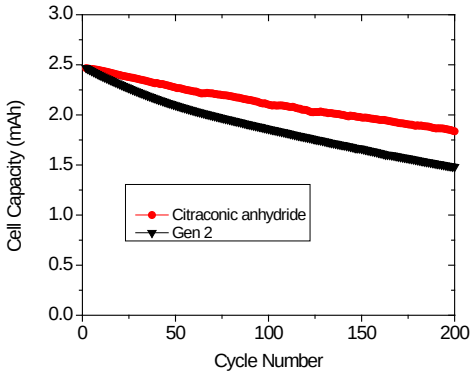


Figure 2. Cell performance for citraconic acid (additive 6) showing improved cycling.

TASK 3.3 - PI, INSTITUTION: Brett Lucht, University of Rhode Island

TASK TITLE - PROJECT: Electrolytes - Development of Electrolytes for Lithium-ion Batteries

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cell performance, life, cost: Calendar life: 40^oC, 15 yrs; Survival Temp Range: -46 to +66^oC; Unassisted Operating & Charging Temperature Range, -30 to + 52^oC.

OBJECTIVES: Develop novel electrolytes with superior performance to SOA ($LiPF_6$ in carbonates). Develop an understanding of the source of performance fade in graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells cycled to high voltage (4.8 V *vs* Li). Develop an electrolyte formulation that allows for superior performance of graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells. Synthesize and characterize novel non-fluorinated Li salts for Li battery electrolytes.

GENERAL APPROACH: Investigate the surface of cathodes and anodes cycled with novel electrolytes, with or without additives, to develop a mechanistic understanding of interface formation and degradation. Develop additives for high voltage (~4.8 V) cathode materials which inhibit performance fade *via* reduction of Mn dissolution or cathode surface passivation. Use novel synthetic methods to prepare non-fluorinated lithium salts for lithium ion battery electrolytes.

STATUS OCT. 1, 2012: $LiPF_4(C_2O_4)$ electrolytes with optimized performance at low temperature after accelerated aging have been investigated. A better understanding of the role of electrolytes in the poor cycling efficiency and capacity fade of Li/$LiNi_{0.5}Mn_{1.5}O_4$ cells has been developed. Novel electrolyte formulations which optimize the performance of Li/$LiNi_{0.5}Mn_{1.5}O_4$ cells cycled to high voltage (4.8 V *vs*. Li) have been designed.

EXPECTED STATUS SEP. 30, 2013: A better understanding of the role of electrolyte in performance fade of graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells will have been developed. This understanding will be used to develop novel electrolyte formulations which improve the performance of graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells. One or more novel non-fluorinated salts will have been synthesized and the performance of the novel salt in electrolyte formulations in graphite/ $LiNi_xCo_{1-2x}Mn_xO_2$ cells will be investigated.

RELEVANT USABC GOALS: Calendar life: 40^oC, 15 yrs; Survival Temp Range: -46–52^oC; Cold cranking power at -30^oC; Cycle life; Peak Pulse Discharge Power, 10 sec.

MILESTONES:

(a) Develop an understanding of the role of electrolyte in capacity fade for graphite/ $LiNi_{0.5}Mn_{1.5}O_4$ full cells cycled at moderately elevated temperature (55^o). (Mar. 13) **On schedule**

(b) Design electrolyte formulations to decrease cell inefficiency (50% of SOA) and decrease capacity fade (50% of SOA) for graphite/$LiNi_{0.5}Mn_{1.5}O_4$ full cells. (Jul. 13) **On schedule**

(c) Synthesize and characterize novel non-fluorinated lithium salts and test novel electrolytes in graphite/$LiNi_xCo_{1-2x}Mn_xO_2$ cells. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

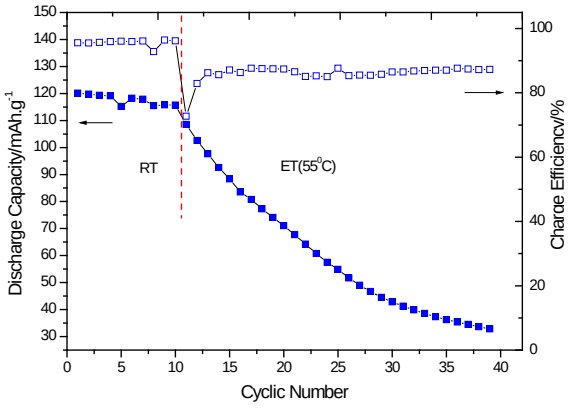


Figure 1. Cycling performance of graphite/ $LiNi_{0.5}Mn_{1.5}O_4$ cell at 25°C (RT) and 55°C (ET).

With regards to milestone (a): Due to significant differences in the observed capacity retention and efficiency of Li/$LiNi_{0.5}Mn_{1.5}O_4$ cells compared to graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells, a detailed analysis of the capacity retention and cycling efficiency of graphite/ $LiNi_{0.5}Mn_{1.5}O_4$ cells cycled to high voltage at moderately elevated temperature are being conducted. Both the anode and the cathode contribute to the capacity loss and impedance rise of graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells cycled at 55°C. The cycling performance of graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells at 25°C is good, but capacity decreases dramatically upon cycling at 55°C. Surface analysis of the cathodes by SEM and XPS indicate that electrolyte decomposition results in the generation of a cathode-electrolyte interface. Thus, the source of the increased impedance may be related to the reaction of electrolyte with the surface of the cathode particles or changes in the crystal structure of the cathode particles at the surface. Capacity loss on the graphite anode is typically reported to be due to continuous dissolution/reformation of SEI film during cycling at 55°C. Surface analysis of the graphite anodes after cycling suggests that the anode SEI is changing and becoming thicker, but the changes to the graphite SEI do not explain the significantly poorer performance of graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells cycled to 55°C. Cross-sectional SEM images clearly indicate that the graphite electrode is delaminating from the Cu current collector. The increased performance loss of the graphite anode is likely related to Mn dissolution and reduction on the anode that may be damaging the anode SEI and contributing to anode delamination.

With regards to milestone (b): Our team is designing electrolyte formulations to optimize the performance of graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells cycled to 4.8 V (*vs.* Li). Preliminary investigations suggest that novel additives improve the performance of graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells at moderately elevated temperature (55°C). Additional investigations are in progress.

With regards to milestone (c): Initial computational investigations of novel non-fluorinated salts for Li-ion battery electrolytes have provided promising results. The LUMO of the novel salt is very similar to that of LiBOB suggesting that it may be a good SEI film forming salt while the HOMO is similar to $LiPF_6$ suggesting good oxidative stability. Synthetic methods are being developed to prepare the novel salt.

Collaborations: D. Abraham (ANL), M. Smart (NASA-JPL), V. Battaglia, G. Chen, and J. Kerr (LBNL), A. Garsuch, M. Payne (BASF), and the High Voltage Spinel Focus Group.

Publication and Presentations: **"**Performance of lithium tetrafluorooxalatophosphate in methyl butyrate electrolytes," *J. Appl. Electrochem.* In Press. "Effect of electrolyte and additives on performance of $LiNi_{0.5}Mn_{1.5}O_4$" Pacific Rim Meeting on Electrochemistry and Solid State Sciences, Honolulu, HI, October 2012. "Effect of electrolyte and additives on performance of $LiNi_{0.5}Mn_{1.5}O_4$" NAAT Batt Annual Meeting and Symposium, Austin, TX, January 2013.

TASK 3.4 - PI, INSTITUTION: Daniel Scherson and John Protasiewicz, Case Western Reserve University

TASK TITLE - PROJECT: Electrolytes ─ Bifunctional Electrolytes for Lithium-ion Batteries

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Abuse tolerance

OBJECTIVES: Design, synthesize, and characterize physical, electrochemical, and interfacial characteristics of functionalized Li-salt anions containing phosphorus moieties known to impart materials with flame retardant properties (Flame Retardant Ions or FRIONs) and additional functional redox active groups capable of providing overcharge protection. Develop and implement ATR-FTIR spectroscopic methods for monitoring *in situ* products generated at Li-ion battery anodes.

GENERAL APPROACH: Develop methods for the chemical functionalization of anions known to improve the performance of Li-ion batteries with covalently linked groups displaying flame retardant and/or overcharge protection attributes. Establish guidelines for the rational design and synthesis of optimized FRIONs and FROPs based on the analysis of results of testing in actual Li-ion batteries. Develop new *in situ* tactics for the application of attenuated total reflection Fourier transform infrared ATR-FTIR for the characterization of solution products generated at Li-ion battery anodes and solid electrolyte interfaces formed therein.

STATUS OCT. 1, 2012: Complete synthesis and purification of four cyclic triol borate (CTB) salts and determination of their flammability. Development of methods for the preparation of 100g of CTB-type compound for testing in actual batteries finished. Develop methods for depositing a thin layer of metal onto the diamond window for ATR measurements and thus avoid problems with electrolyte contributions due to migration effects of IRAS.

EXPECTED STATUS SEP. 30, 2013: Complete synthesis and characterization of new FRION materials based on diphosphonato-catecholate ligand (DPC) including flammability and electrochemical testing. Scale up synthesis of $Li[B(DPC)_2]$ and Li[B(DPC)(oxalate)] salts for testing in cells. Establish structure-electrochemical performance relationships and comparisons with previously studied anion families. Systematic *in situ* ATR-FTIR spectroscopic and impedance studies involving selected solvent formulations incorporating Case FRIONs both as main salts and additives.

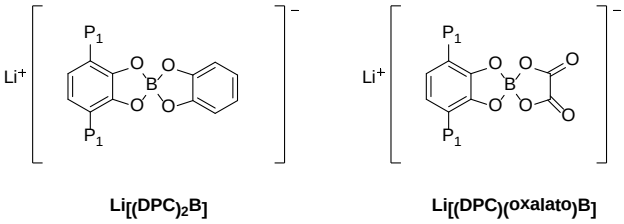
RELEVANT USABC GOALS: No fire or rapid disassembly of cells during abuse conditions.

MILESTONES:

(a) Prepare and fully characterize the electrochemical and flammability properties characteristics of $Li[B(DPC)_2]$ and Li[B(DPC)(oxalate)] salts. (Oct. 12) **Complete**
(b) Expand the $Li[B(DPC)_2]$ and Li[B(DPC)(oxalate)] salts-type libraries of compounds (Mar. 12) **On schedule**
(c) Synthesize and characterize a $Li[P(DPC)_3]$ FRION. (Sep. 13) **On schedule**
(d) Complete characterization of the effect of Case additives by cyclic voltammetry and impedance measurements with the most promising materials as determined from Item (e) below. (Sep 13) **On schedule**
(e) Perform full testing of all Case salts as full fledge electrolytes and/or as additives in actual batteries at Novolyte (Oct 12), and LBNL and ANL. (Sep 13) **On schedule**
(f) Improve cycling by at least 15% to reach the same decay/end of life *vs.* the control electrolyte.(Sep 13) **On schedule**
(g) Construct and optimize cell for *in situ* ATR measurement with metal-coated diamond window. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Synthesis and characterization of FRIONS – Work in this quarter has focused on the full characterization of two diphosphinato-catechol (DPC)-type FRIONs denoted as 617 and 618 in Fig. 1, as well as the synthesis of novel precursors for new type FRIONs, as seen in Fig. 2. Full characterization, including ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy, IR spectroscopy , elemental analysis, thermogravimetric analysis, high resolution mass spectroscopy, X-Ray crystallography, and heat-release testing, has been performed for the DPC-type FRIONs in addition to electrochemical analysis. Flammability tests show a favorable char yield: 42.20% for $Li[(DPC)_2B]$ and 49.60% for Li[(DPC)(oxalato)B]. Heat-release-rate (HRR) data has also been determined for both DPC salts. The total heat release for $Li[(DPC)_2B]$ is 12.17 kJ/g and for Li[(DPC)(oxalato)B] is 8.70 kJ/g. Single crystal X-Ray analysis has confirmed the structure of Li[(DPC)(oxalato)B]. New FRION precursors have been prepared. These molecules have been designed with the intent of varying the FRION backbone structure. Efforts to convert these precursors into lithium borate salts are underway and should result in the target compounds seen in Fig. 2. Performance tests of new FRIONs (Fig. 1) as additives were carried out in 650 mAh 111 NMC cells using 1M $LiPF_6$ in EC/EMC (3:7 by vol) as the base electrolyte. Capacity retention as a function of cycle number plots representing the average of three replicates of each formulation are given in Fig. 3, where D and uD in DX% and uDX% denote dried and undried, respectively, and X the percent FRION added. Although more tests will be required to corroborate the data so far collected, the FRION 617 dried at 1% concentration appears to improve the capacity retention. Additional electrochemical tests are being arranged with ANL.



617 **618**

Figure 1. DPC-type FRIONs.

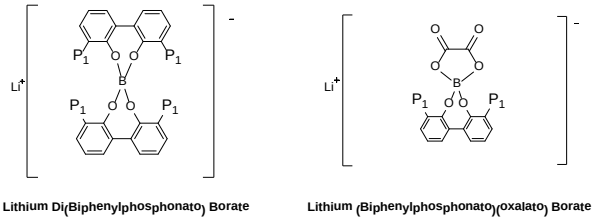


Figure 2. Target FRION salts after precursors are converted into lithium borate salts.

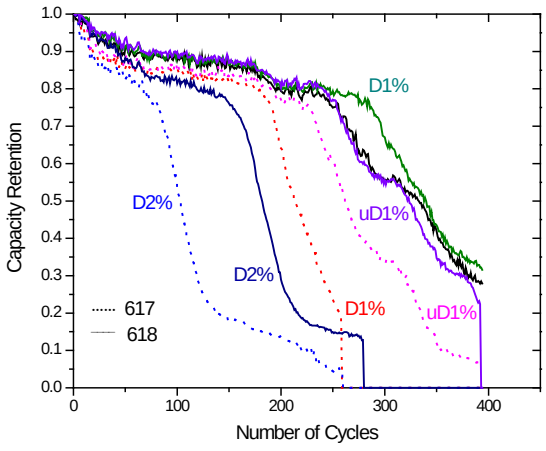


Figure 3. Capacity Retention *vs*. Number of Cycles for two new additives.

TASK 3.5 - PI, INSTITUTION: Austen Angell, Arizona State University
TASK TITLE - PROJECT: Electrolytes – Sulfone Liquids and Sulfate/Triflate Solids for High Voltage Electrolytes
SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)
BARRIERS: Electrolyte needs increased oxidation resistance with decreased ionic resistance, and improved safety. Safety will follow increased ionic liquid or superionic solid content.
OBJECTIVES: To devise new electrolyte types (sulfone mixtures and superionic glasses or plastic solid derivatives) that will permit cell operation at high voltages without solvent oxidation and with adequate overcharge protection, and to provide optimized nanoporous supporting membranes for this electrolyte.
GENERAL APPROACH: The approach has been twofold: (i) A suite of electrolyte studies, beginning with cell-performance testing of additive protected sulfone electrolytes, extending to the design of novel Li^+- conducting media is planned. The latter will retain the high oxidation resistance known for noncyclic sulfones, and conductivity of EC-DMC solutions, but will have Li^+ transport number unity. Novel Li^+-conducting silicon based solid-state conductors and rubbery polymers will be tested for compatibility with the chosen Li (Ni,Mn) spinel cathode. Finally, some novel ionic liquid electrolytes will be tested; and (ii) the further development of the "Maxwell slats" approach to synthesis of nanoporous supports. A hot water-soluble reversibly-self-assembling net has now been abandoned in favor of a successful stronger-bonded model that successfully self-assembles in hot ionic liquid and hydrogen bonding solvents.
STATUS OCT. 1, 2012: Half-cell and full-cell tests with the Li(NiMn) high voltage cathode using our newly developed graphite-compatible all-sulfone, and part sulfone electrolyte solvents, now completed, will begin examination. Progress towards understanding the nature of new Li conducting complex anion solid and liquid-state conductors will have been made. A range of different rigid and non-rigid struts for nano-porous nets (now called amorphous MOFs) will have been explored. Non-calorimetric strategies for determining softening temperatures will have been decided (by collaboration if preferable.)
EXPECTED STATUS SEP. 30, 2013. A go-no-go point will have been passed on sulfone-solvent-based high voltage cell development. An alternative solvent system of even higher voltage window and comparable conductivity, based on "ionic liquid" solvents, will have been tested for performance with the $Li(Ni,Mn)O_4$ cathode, and variants of the superionic glass and metastable crystal variety will have been examined. The best cases of the latter will have been tested with the $Li(Ni,Mn)O_4$ cathode and the expected absence of side reactions verified. The nanoporosity of aqueous self-assembling models of the Maxwell slat concept will have been assessed, and study of more practical (stronger-bonding) variants will have been commenced.
RELEVANT USABC GOALS: 1000 cycles (80% DoD); 10 year life. An electrolyte with electrochemical window 5.2 volts and conductivity 20 mS/cm.
MILESTONES:
(a) Go-no-go on cathode half cells with sulfone electrolytes with HFiP additive. (Feb. 13) **On schedule**
(b) Production of new plastic Li-conducting phases of σ(25ºC) >10 mS/cm. (Jun. 13) **On schedule**
(c) Achievement of glassy or viscous liquid single-ion Li-conducting versions of (b). (Jun. 13) **On schedule**
(d) Production of new mixed 3 and 4-bonding covalent nanoporous nets (amorphous MOFs.) (Jun. 13) **On schedule**
(e) Go-no-go development of mechanically robust nanoporous covalent networks for novel solution and plastic alkali-ion conductors. (Aug. 13) **On schedule**

PROGRESS TOWARD MILESTONES

(a) **Go-no-go on cathode half cells with sulfone electrolytes with HFiP additive - Feb. 2013**. In earlier reports it was noted, that although the sulfone solvents set out to be developed were very satisfactory at graphite electrodes, their performance at the LNMO was unsatisfactory, for reasons assumed to be due to poor SEI-forming ability. The judgment was based on apparent irreversibility in Li/EMS-FMS-$LiPF_6$/LNMO cyclic voltammograms. However, study of coin cells on a recently purchased battery tester has given reason for more optimism. The FMS is a low-viscosity, low-dielectric constant solvent that plays the role of DMC in the standard carbonate electrolyte. While the coulombic efficiency is lower than the cells containing the standard electrolyte, the cyclability seems good. The two steps in the charging potential are clearly seen. Further testing using some recommended additives will now be carried out.

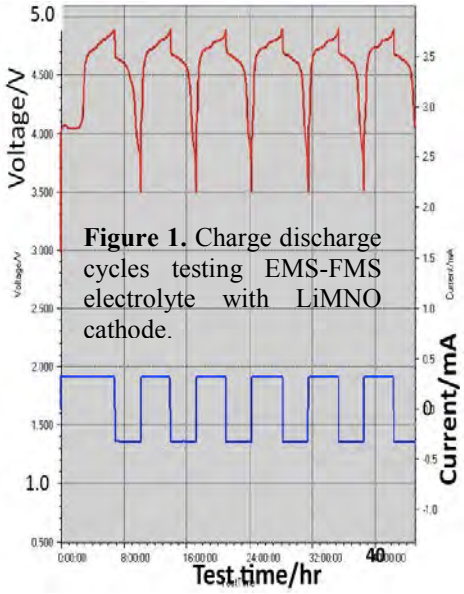


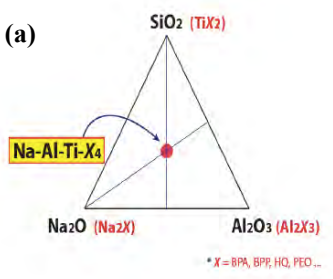
Figure 1. Charge discharge cycles testing EMS-FMS electrolyte with LiMNO cathode.

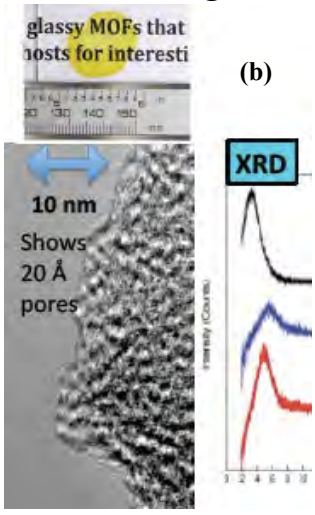
(b) **Production of new plastic Li-conducting phases of σ(25ºC) >10 mS/cm – Jun. 2013**

Refinements of the synthetic techniques are being made to establish better controls on the plastic crystal products for which promising results have been reported in the previous quarter. Our aim is to provide a completely closed system for the preparation. Provision of internal traps for gaseous products have caused some developmental problems.

(c) **Achievement of glassy or viscous liquid single ion Li-conducting versions of (b) by June 2013.** Glasses and crystals have the advantage of extreme resistance to oxidative breakdown due the immobility of all species except the alkali metal**.** However, work on glasses has been put on hold while the more promising plastic crystal conductors (b) above are being pursued.

(d) **production of new mixed 3 and 4-bonding covalent nanoporous nets (amorphous MOFs) by June 2013.**





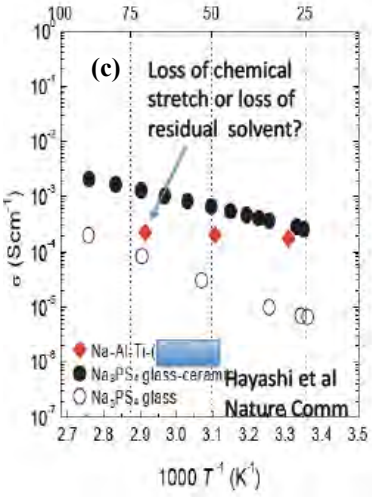


Figure 2. (a) location of target compound in ternary diagram **(b)** structural details, TEM, XRD **(c)** conductivity.

The lattice of the well-known mineral $NaAlSiO_4$ (containing trivalent Al^{3+} compensated Na^+) has been "chemically stretched" by replacing the oxygen (Fig. 2(a) with a divalent chemical slat, **X**. This results in a nanoporous ***glassy*** material with 20-25Å cavities [see Fig. 2 (b)] that accept solvents. Solvents lubricate the movement of Na^+ ions, resulting in ***single ion conductivity*** superior to the best glassy materials (see Fig. 2(c))

(e) **go/no-go development of mechanically robust nanoporous covalent networks for novel solution and plastic alkali-ion conductors by August 2013.** (on schedule see (d)).

BATT TASK 4

CATHODES

Task 4.1 - PI, INSTITUTION: Michael Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes – Novel Cathode Materials and Processing Methods

SYSTEMS: Conoco Philips CPG-8 Graphite/1M $LiPF_6$+EC:DEC(1:2)/Toda NMC
Conoco Philips CPG-8 Graphite/High voltage electrolyte/Li-Ni-Mn-O spinel

BARRIERS: Low energy, cost and abuse tolerance limitations of Li-ion batteries

OBJECTIVE: To develop low cost, high-energy and high-power Mn-oxide-based cathodes.

APPROACH: Li_2MnO_3-stabilized composite electrode structures, such as 'layered-layered' $xLi_2MnO_3 \bullet (1-x)LiMO_2$ (M=Mn, Ni, Co), 'layered-spinel' $xLi_2MnO_3 \bullet (1-x)LiM_2O_4$ and more complex 'layered-layered-spinel' $y\{xLi_2MnO_3 \bullet (1-x)LiMO_2\} \bullet (1-y)LiM_2O_4$ systems are receiving international attention because they can provide rechargeable capacities between 200 and 250 mAh/g between 4.6 and 2.0 V *vs*. Li. These electrodes suffer from voltage decay and surface instability on cycling, thereby compromising the energy and power of the Li-ion cells and preventing their implementation in practical systems. A novel, simple, and versatile processing technique, using Li_2MnO_3 as a precursor, to synthesize composite electrode structures is advocated; it offers the possibility of tailoring composite electrode structures and enhancing their electrochemical properties to meet Li-ion battery performance targets for PHEVs and EVs.

STATUS OCT. 1, 2012: Significant progress in exploiting a new synthesis approach using Li_2MnO_3 as a precursor to fabricate high-capacity (200-250 mAh/g), structurally-integrated lithium-metal-oxide composite electrode materials, such as 'layered-layered', 'layered-spinel', 'layered-rocksalt' systems and more complex types, was made in FY 2012. The project focused predominantly on evaluating detailed structural, electrochemical, and surface properties of 'layered-layered' electrodes; the structural information was obtained from experiments conducted at Argonne's Advanced Photon Source.

EXPECTED STATUS SEP. 30, 2013: Progress will be made in enhancing the electrochemical and structural stability of 'layered-layered' $xLi_2M'O_3 \bullet (1-x)LiMO_2$ electrodes at high potentials, with improvements in rate capability and cycle life.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

(a) Identify at least three promising, high-capacity (200-250 mAh/g) $xLi_2M'O_3 \bullet (1-x)LiMO_2$ compositions with a high Mn content using Li_2MnO_3 or $LiMn_{0.5}Ni_{0.5}O_2$ as a precursor, determine their structures, and evaluate their electrochemical properties. (Sep. 13) **On schedule**

(b) Improve the surface stability of the electrode materials at high charging potentials by coating methodologies. (Sep. 13) **On schedule**

(c) Model surface structures and interfacial phenomena of coated electrodes. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Collaborators: Jason Croy, Brandon Long, Mahalingam Balasubramanian, Kevin Gallagher

Milestone (a) addressed: Evaluate the electrochemical properties of $xLi_2M'O_3 \bullet (1-x)LiMO_2$ ('layered-layered') electrode structures with a high Mn content.

Lithium- and manganese-rich, $xLi_2MnO_3 \bullet (1-x)LiMO_2$ (M = Mn, Ni, Co) 'composite' electrodes (LMR-NMC) represent one of the most promising options for advanced, high-energy-density Li battery products. Li_2MnO_3 plays a key role as an integrated component in LMR-NMC structures, serving as a reservoir for extra Li that can be translated into capacity. The Li reservoir is also important for stabilizing the electrode structure and dictates the operating voltage window for optimum performance. In order to better understand the important role of the Li_2MnO_3 component during electrochemical cycling, a systematic study of $xLi_2MnO_3 \bullet (1-x)LiMn_{0.5}Ni_{0.5}O_2$ electrodes with x = 0, 0.1, 0.3, and 0.5 was initiated. Figure 1 shows the electrochemical cycling data for a sample with x = 0.3 in a Li half-cell at 30°C; the sample was initially activated to 4.7 V at 10 mA/g before being subjected to three consecutive window-opening cycles conducted at a 5 mA/g rate (Fig. 1a). Figures 1b and 1c show similar, consecutive window-opening experiments conducted at the same rate to monitor changes on extended cycling. The voltage window and cycle number (in parenthesis) of the window-opening experiments are indicated in the top left corner of Figs. 1(a-c).

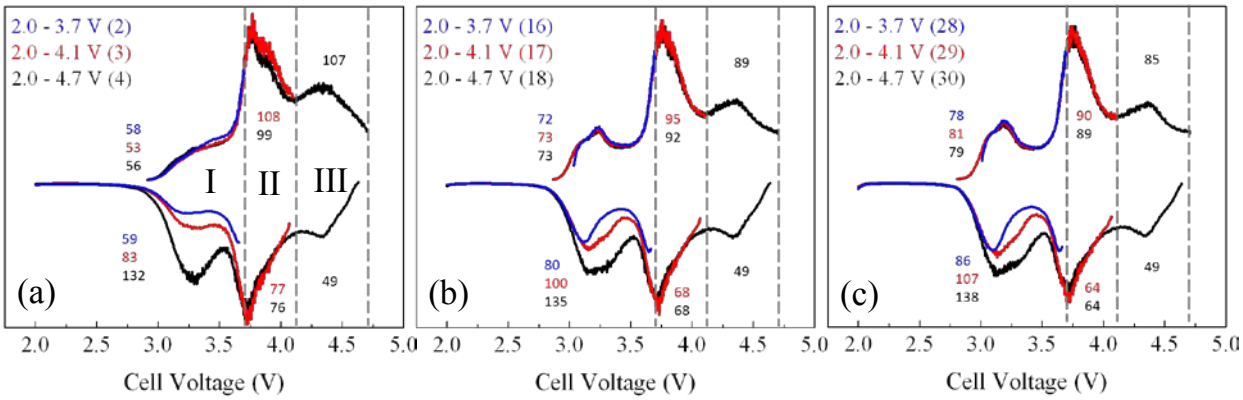


Figure 1. dQ/dV data of three consecutive window-opening cycles obtained during cycles 2-4; 16-18, and 28-30 of a $Li/0.3Li_2MnO_3 \bullet 0.7LiMn_{0.5}Ni_{0.5}O_2$ cell.

The dQ/dV data in Fig. 1 can be divided into three regions, defined by the dashed lines and labels, I, II and III in Fig. 1a. The numbers in each region denote the capacity (mAh/g) obtained in the window during charge and discharge and are color-coded to the legend provided in the top left corner of each figure. There are significant discrepancies between the charge and discharge capacities, particularly in the 2.0 to 4.1 V and 2.0 to 4.7 V windows. In addition, the discharge capacity in region III, for the 2.0 to 4.7 V windows in Figs. 1(a-c), remains constant over long-term cycling. It therefore appears that the excess capacity gained in region III, when charging to high potentials, is not recovered on discharge until a voltage of <3.7 V, is reached[1]. The data verify that the observed hysteresis is an inherent property of this class of materials and that the excess capacity obtained during charge in region I can be directly related to voltage fade.

Reference

1. J.R. Croy, K.K. Gallagher, M. Balasubramanian, Z. Chen, Y. Ren, D. Kim, S.-H. Kang, D.W. Dees, and M.M. Thackeray, *J. Phys. Chem.* C, DOI: 10.1021/jp312658q, (2013).

TASK 4.2 - PI, INSTITUTION: Marca Doeff, Lawrence Berkeley National Laboratory

TASK TITLE: Cathodes – Design of High Performance, High Energy Cathode Materials

SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cost, power and energy density, cycle life

OBJECTIVES: To develop high energy, high performance cathode materials including composites and coated powders, using spray pyrolysis and related synthesis techniques.

GENERAL APPROACH: High-energy cathode materials such as modified NMCs and $LiNi_{0.5}Mn_{1.5}O_4$ (LNMS) are synthesized *via* spray pyrolysis and related techniques, as well as composites containing these materials, and coated particles. For comparison, materials are also made by conventional techniques such as solid-state synthesis and the mixed hydroxide method. An array of physical and electrochemical techniques is used to characterize their behavior, in conjunction with members of the diagnostics team. Emphasis is placed on increasing energy density without sacrificing stability, safety, or cycle life.

STATUS OCT. 1, 2012: Phase-pure samples of $LiNi_{0.5}Mn_{1.5}O_4$ spinel (LNMS) have been produced by spray pyrolysis, and work on composite materials has begun. The survey of Li[Ni, Co, Ti, Mn]O_2 compounds was completed, allowing selection of the most promising compositions for further work to be carried out.

EXPECTED STATUS SEP. 30, 2013: Synthetic parameters for producing hollow LNMS particles (useful for making composites) and solid particles (for coated materials) will have been worked out. Work on NMCs will be directed towards understanding the mechanism of improvement in capacities and cycling behavior observed in some compounds when Ti is partially substituted for Co.

RELEVANT USABC GOALS: High energy, thermal stability, cycle life, cost (EV, PHEV).

MILESTONES:

(a) Synthesize and electrochemically characterize composites consisting of spray-pyrolyzed LNMS hollow particles containing and coated with $LiFePO_4$ or a manganese oxide spinel.(Sep. 13) **On schedule**

(b) Produce and electrochemically characterize thin-film electrodes of a high-energy Ti-substituted NMC suitable for synchrotron studies. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

1) *In situ* synchrotron XRD experiments were carried out on Li cells containing a disordered LNMS made by combustion synthesis (Fig. 1) to determine its phase behavior as a state-of-charge. *In situ* experiments on an ordered sample, made the same way but annealed at 700°C, were carried out during a previous quarter and can be used for comparison. (Synchrotron experiments are a collaboration with G. Chen and J. Cabana of LBNL and A. Mehta of SSRL). Cells containing either of these two materials have been cycled at room temperature and 50°C. The ordered material seems to exhibit poorer cycling behavior than the disordered material, even at room temperature. The reasons for this are not known at present, but further analysis of the data may shed light on this. A paper for publication is currently under preparation, and a new postdoctoral associate has been hired to replace Dr. Kinson Kam, who left in November 2012 to start work for Haldor Topsoe in Denmark. Dr. Feng Lin is expected to arrive sometime in February.

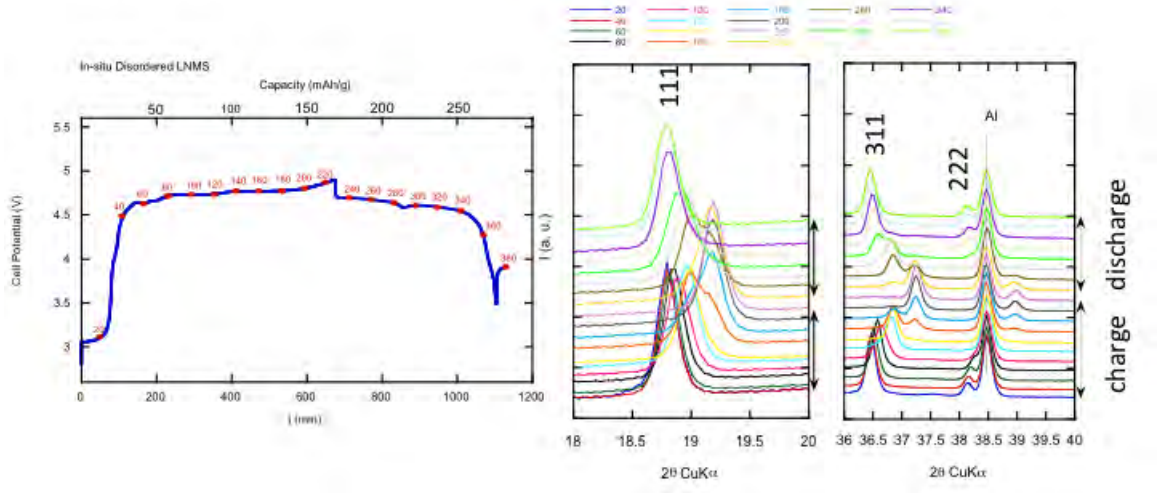


Figure 1. Charge/discharge profile of a Li/disordered LNMS cell used for an *in situ* synchrotron XRD experiment, and selected areas of the XRD patterns obtained during the experiment.

2) A new precursor material, $TiO(SO_4)$, has been used in the mixed hydroxide synthesis of two Ti-substituted NMCs: 442-Ti02 ($Li[Ni_{0.4}Co_{0.18}Ti_{0.02}Mn_{0.4}]O_2$ and 333-Ti03 ($Li[Ni_{0.33}Co_{0.3}Ti_{0.03}Mn_{0.33}]O_2$. This precursor is more stable than the oxynitrate used previously and allows better compositional control. The new materials performed as well as those made with oxynitrate, and also gave higher capacities (~215 mAh/g, using a 4.7 V cutoff) than unsubstituted baseline materials, as was observed previously with Ti-substituted samples. Future plans are to scale up the mixed hydroxide synthesis and give samples to V. Battaglia of LBNL for testing in full cells. Cells with binderless cathodes containing NMCs and Ti-substituted NMCs are also being tested. Binder-free cathodes are needed for synchrotron XPS experiments to compare particle surfaces of NMCs and Ti-substituted NMCs undergoing charge and discharge (with J. Cabana, G. Chen, P.N. Ross, and Z. Liu of LBNL) using ESCA analysis. The goal is to correlate differences in the surface chemistries with the observed increases in discharge capacities for the Ti-substituted cathodes compared to the baseline materials.

TASK 4.3 - PI, INSTITUTION: Arumugam Manthiram, University of Texas at Austin

TASK TITLE - PROJECT: Cathodes – High-capacity, High-voltage Cathode Materials for Lithium-ion Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cost, energy density, power density, cycle life, and safety

OBJECTIVES: To develop (i) low-cost cathodes based on polyanions that can offer a combination of high energy and power with excellent thermal stability and safety, and (ii) low-cost, high-voltage spinel cathodes that can offer high power and energy along with long cycle life.

GENERAL APPROACH: Our focus is on the design and development of cathode materials based on polyanions that have the possibility for reversibly inserting/extracting more than one Li^+ ion per transition metal ion, M^{n+}, and/or operating above 4.3 V. Some example systems to be pursued are Li_2MSiO_4 and $Li_2MP_2O_7$ (M = Mn, Fe, Co, and Ni) and their solid solutions. However, there are technical challenges in achieving the theoretical energy densities of many of these cathode materials. Synthesis and processing conditions play a critical role in realizing the full capacities of these polyanion cathodes with more than one Li^+ ion per M^{n+} ion. Novel solution-based synthesis approaches, such as microwave-assisted solvothermal methods that can offer controlled nanomorphologies, are pursued to maximize the electrochemical performance. The synthesized nanostructured polyanion cathodes are characterized by a variety of techniques including *ex situ* and *in situ* X-ray diffraction, electron microscopy (SEM, TEM, and STEM), X-ray photoelectron spectroscopy, time of flight–secondary ion mass spectroscopy, and in-depth electrochemical measurements. In addition, the role of cation doping, segregation of certain doped cations to the surface, cation ordering, morphology, and surface planes on the electrochemical properties of high-voltage spinel cathodes are investigated. Based on the characterization data gathered, a fundamental understanding of structure-composition-property-performance relationships is developed.

STATUS OCT. 1, 2012: Developed (i) novel synthesis approaches to obtain high-capacity, high-voltage polyanion (silicate and phosphate) cathodes with unique nanomorphologies, (ii) an understanding of the factors that control the performance of high-voltage (4.7 V) spinel oxide cathodes, and (iii) an understanding of their structure-composition-property-performance relationships.

EXPECTED STATUS SEP. 30, 2013: (i) Synthesis by novel solution-based synthetic approaches and characterization of $Li_2MP_2O_7$ (M = Fe, Mn, Co, and Ni) and their solid solutions, as well as Li_2MSiO_4 (M = Mn, Fe, Co, and Ni) and their solid solutions, and (ii) an understanding of the influence of morphology and crystal planes on the performance of high-voltage spinel cathodes.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles, 10-year life, < 20% capacity fade over a 10-year period

MILESTONES:

(a) Understand the influence of morphology and crystal planes on the electrochemical performance of high-voltage spinels. (Dec. 12) **Complete**

(b) Synthesize and characterize $Li_2MP_2O_7$ (M = Fe, Mn, Co, and Ni) as well as their solid solutions. (Jun. 13) **On schedule**

(c) Assess surface segregation in $Li_2M_{1-x}Fe_xSiO_4$ and $Li_2M_{1-x}Fe_xP_2O_7$ (M = Co, Mn, and Ni.) (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

With an aim at increasing the energy density of phosphate cathode materials, three polymorphs of $LiVOPO_4$ were synthesized with a facile, low-temperature microwave-assisted solvothermal process. The triclinic α-$LiVOPO_4$ polymorph was the most stoichiometric. The effect of synthesis conditions on particle size and morphology along with the electrochemical performance were studied in detail. Single-phase samples of α-$LiVOPO_4$ could be formed with several solvent mixtures consisting of water and alcohols/glycols; the smallest particles and best electrochemical performance resulted from synthesis in a mixture of water and glycol. The typical voltage range to cycle $LiVOPO_4$ is between 3.0 and 4.0 V, but by cycling down to 2.0 V instead of 3.0 V, more than one Li could be inserted/extracted by accessing the $V^{3+/4+}$ redox couple between 2.0 and 2.5 V. Of interest, increasing the voltage window to 2.0 to 4.0 V results in a discharge capacity of *ca*. 200 mAh g^{-1}.

In order to develop an understanding of the relationship between cation ordering and morphology, the electrochemical properties below 3 V were examined for materials with identical undoped $LiMn_{1.5}Ni_{0.5}O_4$ compositions but different morphologies. Previously, the most commonly used methods to characterize the degree of cation ordering in the high-voltage $LiMn_{1.5}Ni_{0.5}O_4$ spinel cathodes were indirect, qualitative techniques such as comparing the peak intensities in FTIR and finding small superstructure reflections in the XRD patterns. Interestingly, by discharging the cathode down to 2 V, two plateaus were observed under load at *ca*. 2.7 and *ca*. 2.0 V corresponding to the insertion of Li into the 16c sites; the relative length of these plateaus depends on the lattice strain present in the material. This allows for a clear comparison of the degree of cation ordering among samples. As seen in Fig. 1a, the length of the lower plateau at *ca*. 2.0 V decreases in both samples after the annealing treatment at 700°C, indicating an increase in the degree of cation ordering. These results are in line with what has been reported numerous times in the literature, and are further supported by the more qualitative FTIR (Fig. 1b) and XRD (Fig. 1c) analyses. In Fig. 1b, the peak intensities at 620, 475, and 420 cm^{-1} increase after annealing at 700°C, as indicated by the arrows. Additionally, in Fig. 1c the level of cation ordering is further demonstrated by the fact that the $Li_xNi_{1-x}O$ rocksalt phase becomes soluble in the main spinel phase after annealing, and the superstructure reflections at 45° and 57° are present. The deep electrochemical discharge technique is thus a powerful tool for characterizing the relative degree of cation ordering in the 16d sites of spinel materials.

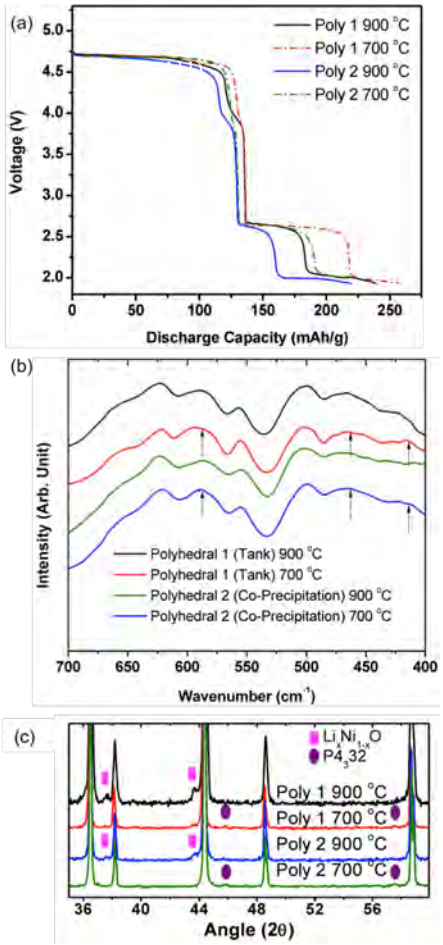


Figure 1: (a) Discharge profiles of spinel $LiMn_{1.5}Ni_{0.5}O_4$ cathodes prepared by two different methods, (b) FTIR analysis, and (c) XRD showing a decrease in $Li_xNi_{1-x}O$ impurity and superstructure reflections after annealing at 700°C.

Reference: Chemelewski, K.R.; Shin, D.W.; Li, W.; Manthiram, A. *J. Mater. Chem. A*, in press.

TASK 4.4 – PI, INSTITUTION: Ji-Guang (Jason) Zhang and Jie Xiao, Pacific Northwest National Laboratory

TASK TITLE: Cathodes – Development of High Energy Cathode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, high cost, limited cycle life

OBJECTIVES: To develop high-energy, low-cost, and long-life cathode materials.

GENERAL APPROACH: To develop high energy-density cathode materials through cost-effective methods. Appropriate doping, surface treatment, and appropriate electrolytes/additives will be used to improve the electrochemical performances of both high-voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ and Mn-based Li-rich layered composite. The fundamental reaction mechanisms of cathode materials during electrochemical processes will be systematically investigated to understand/address the challenges in these cathode materials.

STATUS OCT. 1, 2012: High-voltage $LiNi_{0.5}Mn_{1.5}O_4$ was synthesized by a facile approach, while the content of disordered phase in the spinel was precisely controlled through reheating, element substitution, or different cooling rates. Several other "inactive" components in the electrode, including cell cans, separators, and carbon additives, were also systematically re-examined for their stability in a high-voltage system. Using the optimized electrolyte and stable components, the high-voltage spinel cathode has achieved more than 500 cycles with less than 20% capacity fade (half cells.) Synthesis of the Li_2MnO_3 baseline has been completed. Surface treatment, doping, and electrolyte additives will be applied in the layered composite system coupled with advanced characterizations to understand/mitigate the degradation issues.

EXPECTED STATUS SEP. 30, 2013: High-energy cathodes for Li-ion battery applications will be further explored. Synthesis of $xLi_2MnO_3 \bullet (1-x)LiMO_2$ (M = Mn, Ni, Co; $0 \leq x \leq 1$) will be optimized and their degradation mechanism will be investigated. Manganese dissolution issue in both layered composite and spinel will be studied and mitigated to improve the cell performance. Appropriate electrolyte additives will be identified in the layered composite system to improve the cycling stability. Safety, power rate, and cycling stability of these cathode materials will be improved to satisfy the need for HEV/EV applications.

RELEVANT USABC GOALS: >96 Wh/kg (for PHEVs), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

MILESTONES:

(a) Identify the key factors related to the oxygen release in layered composite $xLi_2MnO_3 \cdot (1-x)LiMO_2$ (M = Mn, Ni, Co; $0 \leq x \leq 1$). (May 13) **On schedule**

(b) Demonstrate the effects of different treatments (doping, coating, and electrolyte additive) on cathode and improve their cyclability by more than 20% as compared with untreated samples. (Sep. 13) **On schedule**

(c) Identify electrolyte additives that can improve the cycling stability of layered composite to more than 200 mAh/g in 100 cycles at C/3 rate. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

In the last quarter, the electrochemical performances of Li_2MnO_3, which is the initiator for the oxygen release and irreversible capacity loss in lithium-manganese rich layered-layered materials, was reported. Also studied were the electrochemical performance of $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ prepared by ANL and PNNL. While still optimizing the synthesis parameters used in the preparation of layered-layered composites, the effects of an electrolyte additive that can improve its cycling stability is reported.

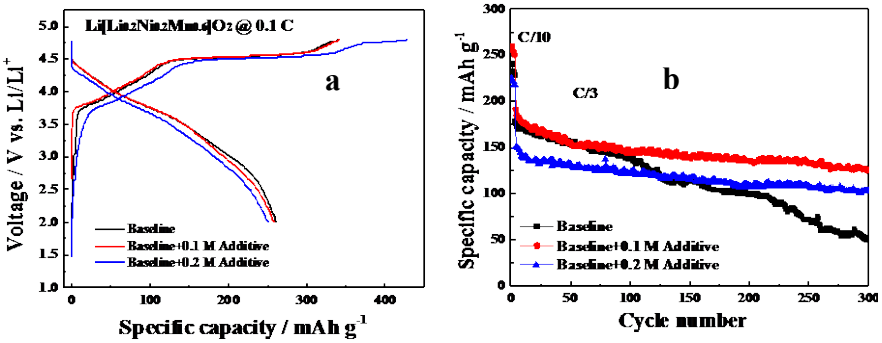


Figure 1. Comparison of a) the first charge-discharge curves and b) cycling ability of $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ layered composite with and without electrolyte additive (2.0-4.8V)

Figure 1 shows the electrochemical properties of $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$-layered composite with or without the electrolyte additive. Compared with the base electrolyte (1M $LiPF_6$ in EC:DEC (1:1 in volume ratio), the addition of 0.1 M additive did not change the amount of the released oxygen or the electrochemical kinetics (as seen by the similar charge curves in Fig.1a). However, addition of the additive significantly improved the cycling stability of the cell as demonstrated in Fig.1b. Without the additive, the capacity from $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ decays rapidly, especially after 100 cycles. After the addition of only 0.1 M additive in the base electrolyte, the cycling performance of the cathode was greatly improved (Fig.1b). While the detailed mechanism of the additive is still under investigation, the hypothesis is that the additive is involved in a surface modification process of the electrode during charge that improves the interfacial properties between the electrode and electrolyte. Excess additive present in a 0.2 M concentration was found to oxidize at above 4.7 V (Fig.1a). In addition, the excess additive lowered the reversible capacity of $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ (Fig.1b), which may be related to a thickening of a passivation film on the cathode surface and increased the cell impedance. Therefore, 0.1 M was chosen as the optimized concentration for this type of additive for the layered-composite cathode. More electrochemical evaluations and characterizations will be performed to unravel the fundamental mechanisms of these interfacial phenomena.

Collaborations: Drs. K. Amine and I. Belharouak at ANL for supplying layered composite cathode; Dr. X.-Q. Yang at BNL for XRD characterizations; Prof. M.S. Whittingham at SUNY Binghamton for characterization.

Publication and presentations:

1. "Surface and structural stabilities of carbon additives in high voltage lithium ion Batteries," Jianming Zheng, Jie Xiao, Wu Xu, Xilin Chen, Meng Gu, Xiaohong Li, Ji-Guang Zhang, *Journal of Power Sources*, **227**, 211-217 (2013).
2. "Formation of the Spinel Phase in the Layered Composite Cathode Used in Li-Ion Batteries," Gu M, Belharouak I, Zheng J, Wu H, Xiao J, Genc A, Amine K, Thevuthasan S, Baer DR, Zhang JG, Browning ND,Liu J, Wang C., ACS Nano. 2012 Dec 18.
3. "High Voltage Li-ion Batteries" Jie Xiao, Jianming Zheng, Xilin Chen, Wu Xu, and Jason Zhang, 222th ECS Meeting, PRiME - Honolulu, Hawaii, **2012**.

Task 4.5 - PI, INSTITUTION: Jordi Cabana, Lawrence Berkeley National Laboratory

TASK TITLE: Cathodes – Novel and Optimized Phases for High Energy Density Batteries.

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low-energy density, poor cycle life, safety

OBJECTIVE: Enable higher density Li-ion batteries through an increase in operation voltage and capacity of the cathode. Design electrode structures that maximize active material utilization and charge density. Understand the structure-composition-properties relationship for bulk and surface in electrodes. Identify new compounds containing non-oxide or polyanions in their crystal structure that are electrochemically active.

GENERAL APPROACH: Employ and develop a variety of synthetic methods to produce materials with controlled purity, crystal structure, and particle morphology. Use spectroscopic and diffraction techniques to monitor the reactions involved in battery electrodes. Explore chemical spaces in search for new phases that may provide performance improvements.

STATUS OCT. 1, 2012: A series of annealed $LiNi_{1/2}Mn_{3/2}O_4$ was produced, analyzed by spectroscopy and diffraction, and their performance was correlated with crystal-chemical parameters. The role of oxide additives on the extent of irreversible reactions has been assessed. A new project, focused on the discovery of new fluoride-containing phases as stable high voltage high capacity Li battery cathodes, was initiated.

EXPECTED STATUS SEP. 30, 2013: A systematic study of the interactions between $LiNi_{1/2}Mn_{3/2}O_4$ surfaces and the electrolyte will be performed. The correlation between crystal-chemistry in $LiNi_{1/2}Mn_{3/2}O_4$ and the phase transformation of the electrode will have been studied. Screening of Li-M-O-F (M=Mn, Fe, Cu) spaces in search for unreported phases will be performed through direct high temperature synthesis and low temperature fluorination.

RELEVANT USABC GOALS: 40-mile PHEV: Energy/Weight 96 Wh/kg; CD Cycle Life 5000 cycles; Calendar Life @ 40°C 15 years.

MILESTONES:

(a) Complete *in operando* X-ray diffraction study of at least 4 samples of $LiNi_{1/2}Mn_{3/2}O_4$ with different degrees of order/disorder. (Mar. 13) **On schedule**
(b) Develop a synthetic protocol for the extensive fluorination of Li-M-O (M=Mn, Fe, Cu) using low temperature treatments. (Apr. 13) **On schedule**
(c) Synthesize at least two new Li-M-O-F (M=Mn, Fe, Cu) using direct high-temperature methods. (Sep. 13) **On schedule**
(d) Determine changes during cycling of the surface chemistry of $LiNi_{1/2}Mn_{3/2}O_4$ depending on coatings and doping, in coordination with the *Spinel Focus Group*. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

During the 1st Quarter of FY13, progress was made toward Milestone (c). *In operando* XRD experiments were conducted at beamline 11-3 at the Stanford Synchrotron Radiation Lightsource (SSRL) on selected $LiNi_{0.5}Mn_{1.5}O_4$ samples within the collection prepared in FY12 (*e.g.*, see Q2 FY12 report). The selection was made based on the degree of Ni/Mn ordering shown by the samples, as probed by NMR, neutron diffraction, and electrochemical signatures. The goal was to identify the origin for the significant difference in rate capability with crystallographic ordering (Q2 FY12). Figure 1a shows a representative set of XRD patterns for a sample with the highest degree of disorder. A series of reversible phase transitions were observed. The results are summarized in Fig. 1b. The early stages of delithiation occur through a solid solution mechanism, followed by consecutive two-phase transitions. In contrast, the sample with the highest degree of ordering shows no discernible solid solution domains (Fig. 1c). The formation of a solid solution leads to a significant reduction in volume change between the phases involved in the first biphasic transition. It is hypothesized that such lower volume change results in smaller strain buildup in the active material particles during this step, thereby increasing the rate of reaction that can be achieved. Two more samples with intermediate extents of ordering are currently under evaluation to confirm the direct dependence between crystal structure and delithiation mechanism, as well as between mechanism and rate performance.

Collaborations this quarter: Prof. Grey (Cambridge), Drs. Persson and Chen, (LBNL), Dr. Casas-Cabanas (CIC Energigune, Spain), Prof. Whittingham (SUNY Binghamton).

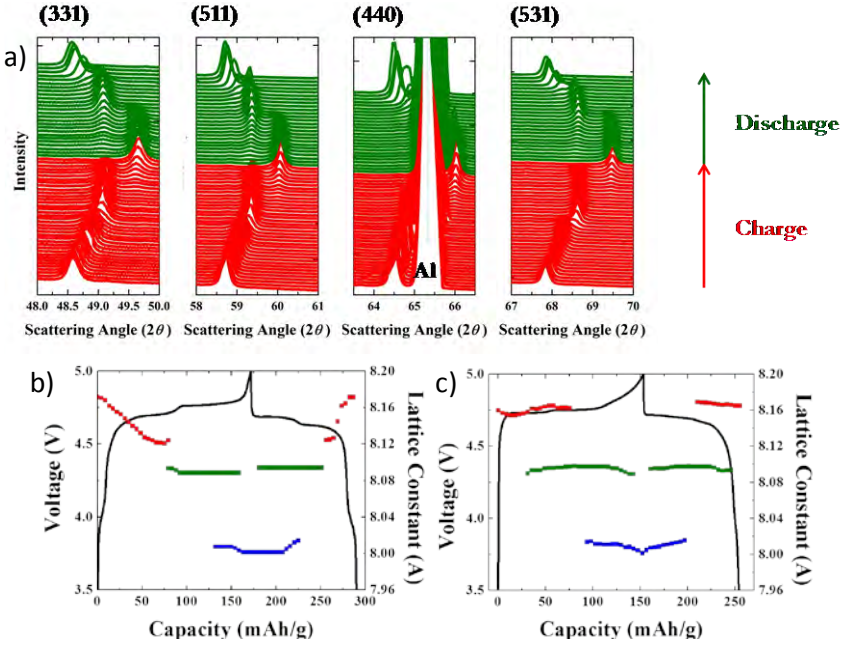


Figure 1: a) Selected *in operando* XRD patterns of $LiNi_{0.5}Mn_{1.5}O_4$ with the highest level of Ni/Mn disorder; b) summary of results in a); c) summary of *in operando* XRD results for a sample with the highest level of ordering.

Publication and Presentations this quarter:

- 2 oral presentations (1 invited) at PRiME 2012, October 7-12, 2012, Honolulu, HI (USA).
- J.B. Cook, C. Kim, L. Xu, J. Cabana, *J. Electrochem. Soc.*, **160**, A46 (2013).

Task 4.6 - PI, INSTITUTION: Patrick Looney and Feng Wang, Brookhaven National Laboratory

TASK TITLE: Cathodes – *In situ* Solvothermal Synthesis of Novel High Capacity Cathodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density and cost

OBJECTIVE: Develop low-cost cathode materials that offer high energy density (>660 Wh/kg) and electrochemical properties (cycle life, power density, safety) consistent with USABC goals.

GENERAL APPROACH: Our approach is to develop and utilize a specialized *in situ* reactor designed to investigate synthesis reactions in real-time using synchrotron techniques. This capability will allow us to identify intermediate or transient phases and better control phase nucleation, reaction rates, and material properties. These new tools and insights will be used to prepare novel high energy density lithium cathode materials (≥660 Wh/kg).

STATUS OCT. 1, 2012: In FY12 work was initiated on the synthesis and electrochemical testing of the high capacity cathode $Cu_{0.95}V_2O_5$. By the end of FY12 a synthesis procedure for the preparation of pure, nano-scale $Cu_{0.95}V_2O_5$ was identified and electrochemical testing was performed. The development of an improved *in situ* synthesis reactor for synchrotron studies and a 2nd generation reactor is complete.

EXPECTED STATUS SEP. 30, 2013: In Year 2 investigation of Cu-V-O compounds will continue. By the end of FY13 multiple Cu-V-O compounds will have been synthesized. The optimal procedure for the synthesis of $Cu_{0.95}V_2O_5$ will be determined by evaluating a variety of precursors (Cu source, V source and reducing agents) and reaction conditions (temperature and time). Electrochemical studies (*in situ* and *ex situ*) along with material characterization (*e.g.,* particle size and morphology) will be determined to identify mechanism(s) of capacity fade. The feasibility of using ion exchange reactions will also be determined.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 3000 cycles (PHEV 40 mile requirement); lower cost batteries.

MILESTONES:

(a) Determine optimal procedure for the synthesis of $Cu_{0.95}V_2O_5$. This will involve an evaluation of precursors, reducing agents and synthesis conditions. (Jan. 13) **Complete**
(b) Identify mechanism(s) responsible for poor cycling in $Cu_{0.95}V_2O_5$ and identify a pathway for reducing capacity fade with cycling. (Mar. 13) **On schedule**
(c) Synthesize and electrochemically characterize at least one other Cu-V-O compound using hydrothermal/solvothermal and/or ion-exchange reactions. (May. 13) **On schedule**
(d) Determine the feasibility of using hydrothermal and/or ion-exchange reactions to prepare polyanion cathodes. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Among the wide variety of Cu-based vanadium oxides, ε-$Cu_{0.95}V_2O_5$ (ε-CVO) is one that has potential application as a cathode material due to its high capacity (~700 Wh/kg). Building on our previous work that identified several approaches for making ε-CVO materials, the effort in this quarter was focused on optimizing the synthesis procedures by evaluating the precursors, reducing agents, and reaction conditions, with a goal to improve the phase purity and crystallinity. The evaluation was performed in *real time* using our developed *in situ* hydrothermal synthesis method.

Figure 1 shows one of the results of *in situ* synthesis of ε-CVO. Using $Cu(NO_3)_2{\cdot}3H_2O$ and V_2O_5, the same precursors used to synthesize β-$Cu_{0.36}V_2O_5$ nano-rods (reported last quarter), the ε-CVO phase in a capillary reactor was obtained by tuning the Cu/V ratio and the concentration of the reducing agent at a temperature as low as 180°C. The intermediate phase, $Cu_3(OH)_2V_2O_7{\cdot}2H_2O$, was found to be a crucial step towards forming the desired final product. This phase was stable at low temperatures and, depending on the concentration of the reducing agent, either transformed into the pure ε-CVO phase or a mixture with others (α-CuV_2O_6, Cu, …) at high temperatures. With the information on the reaction paths gained in *in situ* structural studies, optimal reaction conditions and the ability to 'dial in' the desired phases was obtained.

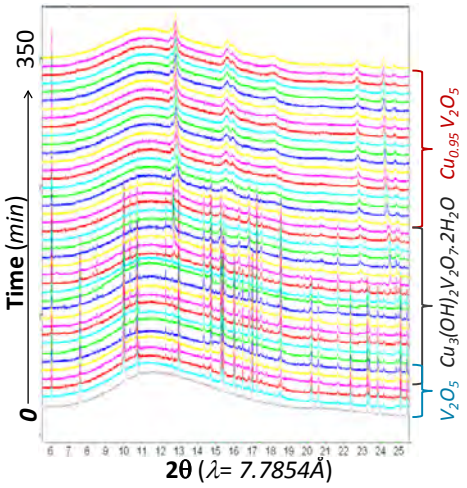


Figure 1. Time-resolved XRD patterns acquired during *in situ* synthesis of ε-CVO.

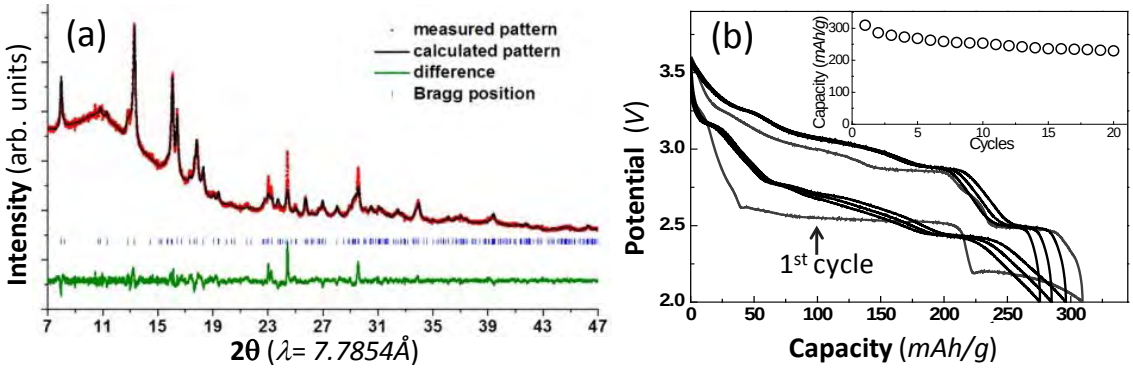


Figure 2. Structure and electrochemical properties of the ε-CVO (a) XRD pattern and refinement; (b) galvanostatic cycling profiles and cyclability (inset) at a rate of C/20 between 3.6-2.0 V.

After determining the optimal reaction conditions and process, a large amount of ε-CVO powder was synthesized in an autoclave reactor for further property evaluation. The powder was examined with synchrotron XRD and shown to have a high degree of crystallinity and purity (Fig. 2a). Excellent electrochemical performance was achieved in the ε-CVO electrodes with a higher percentage of carbon black (~40%), including a high capacity (~300 mAh/g) and reasonable cycling stability at a moderate rate, C/20 (Fig. 2b).

Milestone (a) was successfully completed. The plan is to continue to develop synthesis procedures to tailor the particle size and morphology of ε-CVO that may further improve the electrochemical performance.

Collaborations: Peter Khalifah (Stony Brook University) on synthesis.

Task 4.7 - PI, INSTITUTION: Jim Kiggans and Andrew Kercher, Oak Ridge National Laboratory

TASK TITLE: Cathodes – Lithium-bearing Mixed Polyanion (LBMP) Glasses as Cathode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cathodes for Li-ion batteries require lower cost materials and improved energy density, safety, and cycling stability.

OBJECTIVE: Develop lithium-bearing mixed polyanion (LBMP) glasses as potential cathode materials for Li-ion batteries with superior performance to lithium iron phosphate for use in electric vehicle applications. Modify compositions of LBMP glasses to provide higher electrical conductivities, higher redox potentials, and higher specific energies than similar crystalline polyanion framework materials. Test LBMP glasses for performance and cyclability. The final goal is to develop LBMP glass compositions with the potential to provide specific energies up to near 1000 mWh/g.

GENERAL APPROACH: The experimental approach combines: (1) structure and property modeling, (2) glass processing, (3) glass characterization, (4) conventional cathode production, and (5) electrical and electrochemical testing. Computer modeling will be used to suggest the most promising LBMP glass compositions in terms of electrochemical performance and glass processing capability. Classical heat-quench glass forming and sol gel processing will be used to make the LBMP glasses. Electrochemical performance will be demonstrated on coin cells with LBMP glass cathodes using cycle testing and variable discharge rate testing.

STATUS OCT. 1, 2012: An experimental test matrix for initial cathode glass compositions has been developed. Materials and equipment have been purchased for initial glass compositions. Initial work with TGA-DTA analyses of glass precursors is in progress.

EXPECTED STATUS SEP. 30, 2013: One or more promising glass compositions will be selected from an initial experimental screening. CALPHAD simulation will be developed and verified against initial experimental results. Optimization and examining the interrelation of properties, compositions, and synthesis methods will be underway.

RELEVANT USABC GOALS: Reduce the cost of electrochemical energy storage by developing Li-ion batteries and other advanced energy-storage technologies that afford higher energy densities without sacrificing safety and performance.

MILESTONES:
(a) Setup CALPHAD database and perform initial simulation for one glass composition. (Jan. 13) **Complete**
(b) Synthesize, characterize, and perform electrochemical testing on at least four different glass compositions. (Sep. 13) **On schedule**
(c) Create CALPHAD thermodynamic database and verify results with comparison to initial experimental glass compositions and electrochemical performance. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Thermodynamic models for the baseline glass materials, $FePO_4$ and $Fe_4(P_2O_7)_3$, have been developed through the CALPHAD approach. Thermodynamic descriptions for the crystalline solid and liquid phases of constituent Fe_2O_3 and P_2O_5 have been taken from the SGTE (Scientific Group Thermodata Europe) Substance Database and used as reference states. Thermodynamic model parameters for $FePO_4$ and $Fe_4(P_2O_7)_3$ have been self-consistently evaluated to reproduce the Fe_2O_3-P_2O_5 pseudo-binary phase diagram reported in the literature. From the developed thermodynamic database, the open circuit voltage of crystalline Li/$FePO_4$ has been predicted by calculating the chemical potential of Li. The generated thermodynamic descriptions for the liquid $FePO_4$ and $Fe_4(P_2O_7)_3$ in this quarter then will be combined with those of solid phases to model thermodynamics of their glass phases.

Two baseline glass cathode compositions have been synthesized, characterized, and electrochemically tested. The baseline glass, named FP-03A, has a composition of 0.9 Fe_2O_3 • P_2O_5 and was quenched between Cu plates from a 1280°C melt. The baseline glass, named FP-06A, has a composition of $Fe_4(P_2O_7)_3$ and was quenched in a graphite mold from a 1250°C melt (Fig. 1). The glass compositions of FP-03A and FP-06A were chosen for ease of processing and similarity to established crystalline cathode materials (Li/$FePO_4$ and Li_4/$Fe_4(P_2O_7)_3$, respectively).

Figure 1. Photograph of FP-06A melt quenching inside of a graphite mold.

Glass characterization methods have been established and utilized on the two baseline glasses. XRD results showed no evidence of crystalline material in either glass. Inductively-coupled plasma atomic emission spectroscopy confirmed that the desired iron and phosphorous contents were achieved and that the impurity contents from crucibles and quenching methods were small (<1 wt% Al and <0.01 wt% Cu). Differential thermal analyses of FP-03A and FP-06A were used to identify the glass transition temperatures (490 and 495°C, respectively) and glass crystallization temperatures (590 and 651°C, respectively).

Cathode and coin-cell production methods have been demonstrated on the two baseline glasses. Coin cells of the two baseline glasses have been produced and electrochemically tested. The average particle sizes for the spex-milled FP-03A and FP-06A powders were 6 and 3 μm, respectively. Cathodes were produced using traditional slurry casting of carbon black, polyvinylidene fluoride, n-methyl-2-pyrrolidone, and active glass material.

Electrochemical testing of coin cells with FP-03A and FP-06A cathodes showed very low capacities (<1% theoretical capacity) at C/30, as expected based on particle size, lack of carbon coating, and expected glass properties. The iron phosphate glass cathodes were produced for easy comparison with mixed polyanion glasses of similar composition. The electrochemical performance of mixed polyanion glasses should be markedly superior to the baseline glasses and should provide proof-of-principle for the concept of using mixed polyanion glasses as cathodes. Processing of mixed polyanion glasses is underway.

BATT TASK 5
DIAGNOSTICS

Task 5.1 - PI, INSTITUTION: Robert Kostecki, Lawrence Berkeley National Laboratory

TASK TITLE: Diagnostics – Interfacial Processes

BASELINE SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy (related to cost), poor lithium battery calendar/cycle lifetimes.

OBJECTIVES: (i) Establish direct correlations between electrochemical performance of high-energy Li-ion composite cathodes, and surface chemistry, morphology, topology and interfacial phenomena, (ii) improve the capacity and cycle life limitations of Li_xSi anodes

GENERAL APPROACH: Design and employ novel and sophisticated *in situ* analytical methods to address the key problems of the BATT baseline chemistries. Proposed experimental strategies combine imaging with spectroscopy aimed at probing electrodes at an atom, molecular, or nanoparticulate level to unveil structure and reactivity at hidden or buried interfaces and determine electrode performance and failure modes in baseline Li_xSi-anodes and high-voltage LMNO cathodes. The proposed methodologies, *in situ* and *ex situ* Raman, FTIR and LIBS far- and near-field spectroscopy/microscopy, SPM, spectroscopic ellipsometry, SEM, HRTEM, standard electrochemical techniques, and model single particle and/or monocrystal model electrodes will be used to probe and characterize bulk and surface processes in Si anodes and high-energy cathodes.

STATUS OCT. 1, 2012: This is a new project initiated October 1, 2012. Some insight into the mechanism of electrolyte decomposition at the surface of model anode and cathode materials has been gained and its impact on the electrode long-term electrochemical behavior evaluated. The composition and (re)formation dynamics of the surface layer on model monocrystal Sn and Si intermetallic anodes, and on model single particle and composite high-voltage cathodes, were determined using various complementary spectroscopy techniques. A unique strategy involving the use of *in situ* techniques (AFM, ellipsometry, Raman and fluorescence imaging, FTIR and AP-XPS) in conjunction with *ex situ* techniques (XAS, RBS and NRA) were applied to monitor and identify surface processes. Preliminary evaluation of near-field optical spectroscopy and imaging techniques for fundamental interfacial studies of Li-ion systems were carried out.

EXPECTED STATUS SEP. 30, 2013: Insight into the mechanism of surface phenomena on thin-film and monocrystal Sn and Si intermetallic anodes will be gained and their impact on the electrode long-term electrochemical behavior will be evaluated. Comprehensive fundamental study of the early stages of SEI layer formation on polycrystalline and single crystal face Sn and Si electrodes will be carried out. *In situ* and *ex situ* far- and near-field FTIR and Raman spectroscopy will be employed in conjunction with AFM surface imaging to detect and monitor surface phenomena at the intermetallic anodes. Similar experimental methodology will be used to detect and characterize surface and bulk processes in high-voltage (>4.3V) model and composite cathodes.

RELEVANT USABC GOALS: *Cycle life*: 5000 (deep) and 300,000 (shallow) cycles. *Available energy*: 200 Wh/kg. *Calendar life*: 15 years.

MILESTONES:

(a) Resolve SEI layer chemistry of Si model single-crystal anodes (collaboration with the *BATT Anode Group*. (Jul. 13) **On schedule**

(b) Incorporate an *in situ* electrochemical cell into existing ultrafast laser beam delivery/automated translation stage/spectrometer LIBS system. (Aug. 13) **On schedule**

(c) Characterize interfacial phenomena in high-voltage composite cathodes (collaboration with the *BATT Cathode Group*. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

In the first quarter of FY13 work focused mainly on fundamental fluorescence spectroscopy/imaging investigations of interfacial phenomena that occur at different crystal facets/orientations of $LiNi_{0.5}Mn_{1.5}O_4$ single microcrystals. Model $LiNi_{0.5}Mn_{1.5}O_4$ powder samples of different particle morphology were synthesized and provided by Guoying Chen, LBNL (SEM pictures of the pristine powders are shown in Fig. 1). Basic structural properties of these model cathode materials were investigated to conclude that $LiNi_{0.5}Mn_{1.5}O_4$ particles consist of a dominant crystal facet, namely <112> for the platelets (Fig. 1A), and <111> for the octahedrons (Fig. 1B). Carbon- and binder-free electrodes were prepared according to the procedure established in our group in FY12, and they were tested in the EC:DEC 1:2, 1M $LiPF_6$ electrolyte between 3.5 and 5.0 V *vs*. Li/Li^+.

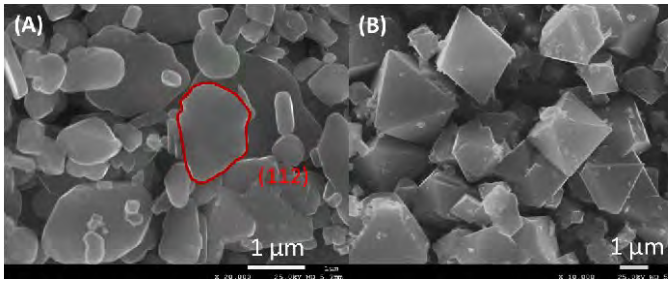


Figure 1. SEM images of $LiNi_{0.5}Mn_{1.5}O_4$ particles (panel A, platelets <112> panel B, octahedrons <111> (courtesy of Guoying Chen, LBNL).

The initial fluorescence response of the model $LiNi_{0.5}Mn_{1.5}O_4$ single-crystal electrodes was similar to the signal observed for a regular polycrystalline material. The fluorescence intensity at the electrode interface always rises at the beginning of the Ni oxidation and then slowly vanishes upon relithiation. Insoluble products of the electrolyte oxidation tend to accumulate at the surface of the electrode contributing to a gradual increase of the fluorescence background signal whereas soluble compounds diffuse away into the electrolyte. Both model electrodes showed a steady increase of the fluorescence background with cycling. However, for the octahedrons the intensity of the fluorescence background remains unchanged after the first cycle whereas fluorescence on the platelets seem to keep growing after every cycle (Fig. 2). This may indicate quite radical differences in surface activity of $LiNi_{0.5}Mn_{1.5}O_4$ depending on material surface orientation. In other words, the steady fluorescence signal from the octahedrons can be associated with the formation of a more stable surface layer on this crystal facet. Further investigations will focus on identification of the fluorescence compounds, their formation mechanism, and possible implications for Li-ion battery systems.

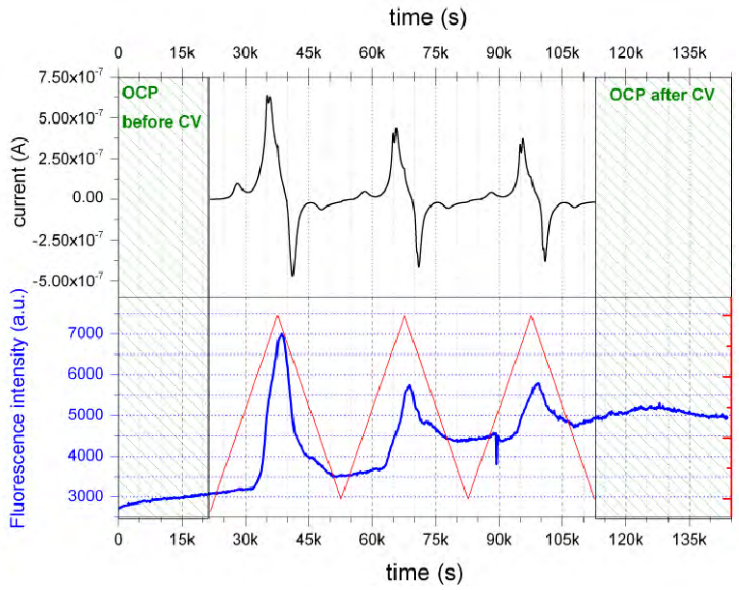


Figure 2. Electrochemical data (top), corresponding integrated fluorescence intensity (bottom-blue) and voltage profile (bottom-red) of $LiNi_{0.5}Mn_{1.5}O_4$ platelet particles in EC:DEC 1:2 1M $LiPF_6$.

To identify basic processes that occur at Si during the initial SEI formation phase, an investigation of electrochemical behavior of Si single crystals was initiated. Basic properties of Si monocrystals with three different surfaces orientations, *i.e.*, <100>, <110> and <111>, will be examined in FY13.

Task 5.2 - PI, INSTITUTION: Xiao-Qing Yang and Kyung-Wan Nam, Brookhaven National Laboratory

TASK TITLE: Diagnostics – Advanced *In situ* Diagnostic Techniques for Battery Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: PHEV: Energy density, Cycle life; HEV: Power density, Abuse tolerance

OBJECTIVE: The primary objective is to determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline in helping the development of high energy density Li battery with better safety characteristics and longer life.

GENERAL APPROACH: To use various synchrotron based X-ray techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. The following approaches will be used: i*n situ* synchrotron XRD and hard XAS at transition metal K-edges during cycling; soft XAS on L-edges of Mn, Ni and Co and K-edges of C, O, and F using electron yield (surface) and fluorescence yield (bulk) detectors after cycle; high resolution transmission electron microscopy (HRTEM) coupled with electron energy loss spectroscopy (EELS) after cycle; *in situ* TR-XRD coupled with MS during heating of charged cathode materials (thermal stability study); *in situ* and *ex situ* Si K-edge XAS of Si based anode materials during cycling; *in situ* quick XAS of the cathode materials for dynamic study during cycling.

STATUS OCT. 1, 2012: This is a new project initiated October 1, 2012. Structural studies on the high energy density Li_2MnO_3-$LiMO_2$ (M = Ni, Mn, Co) layered materials have been carried out (in collaboration with ANL) and *in situ* XRD studies on different types of lithium iron phosphate cathode materials with mesoporous structure. *In situ* XRD and XAS diagnostic studies of high voltage $LiMn_{2-x}M_xO_4$ (M = Ni, Cu etc.,) have also been performed with spinel structure during cycling.

EXPECTED STATUS SEP. 30, 2013: Thermal stability studies of high-voltage $LiMn_{2-x}Ni_xO_4$ with ordered (*P4*$_3$*32*) and disordered (*Fd-3m*) spinel structure will have been carried out using time-resolved XRD coupled with MS and XAS during heating. The XAS studies on high energy density Si-based anode materials during cycles also will have been started.

RELEVANT USABC GOALS: 15-year calendar life, <20% capacity fade over a 10-year period, improved abuse tolerance.

MILESTONES:

(a) Complete the *in situ* time-resolve XRD studies of $LiMn_{2-x}Ni_xO_4$ cathode material with ordered (*P*4$_3$32) spinel structure during heating. (Apr. 13) **On schedule**
(b) Complete the XAS studies of $LiMn_{2-x}Ni_xO_4$ cathode material with ordered (*P*4$_3$32) spinel structure during heating. (Apr. 13) **On schedule**
(c) Complete the *in situ* time-resolve XRD studies of $LiMn_{2-x}Ni_xO_4$ cathode material with disordered (*Fd-3m*) spinel structure during heating. (Sep. 13) **On schedule**
(d) Complete the XAS studies of $LiMn_{2-x}Ni_xO_4$ cathode material with disordered (*Fd-3m*) spinel structure during heating. (Sep. 13) **On schedule**
(e) Complete the *ex situ* Si K-edge XAS studies of Si-based high energy density anode materials after cycles. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

In the 1st quarter of FY13, progress toward milestones was made.

In the first quarter of FY13, BNL focused on changes during heating to the structure of high voltage $LiMn_{2-x}Ni_xO_4$ (LNMO) cathode materials that start with the ordered ($P4_332$) structure using synchrotron-based time-resolved XRD combined with mass spectroscopy.

Increasing the operating voltage is one effective way to increase the energy density of Li-ion batteries, which is very important for PHEVs. The investigation of the thermal stability of structural changes of high voltage $LiMn_{2-x}Ni_xO_4$ cathode materials starting with both ordered ($P4_332$) and disordered (Fd-$3m$) materials is one of our important milestones for FY13.

In situ XRD patterns combined with simultaneously measured mass spectroscopy (MS) data that trace oxygen gas release from ordered LNMO are shown in Fig. 1. The fully-charged, ordered samples take the following structural change route. First, XRD patterns shift toward low angles as the temperature increases, indicating the expansion of the lattice parameter; second, an obvious growth of (220) peak is observed, showing clear evidence of transition metals migrating to the tetrahedral sites in spinel structure; third, a violent structural change occurs accompanied with the beginning of oxygen release. This can be seen from the great broadening of peaks, indicating the well-crystallized structures have been destroyed. At the end of oxygen release, a new phase starts to form as manifested by the growth of peak intensities and sharpening of peak widths. Interestingly, preliminary results on the charged, disordered LNMO suggest that the disordered and ordered LNMO differ in the onset temperature of oxygen release; this be further studied in FY13. The charged, disordered material started to release oxygen at a temperature as low as 210°C, accompanying the abrupt change of XRD pattern. On the other hand, this oxygen release and sudden structural change did not occur for the charged, ordered LNMO up to 250°C, demonstrating better thermal stability of the ordered LNMO over the disordered.

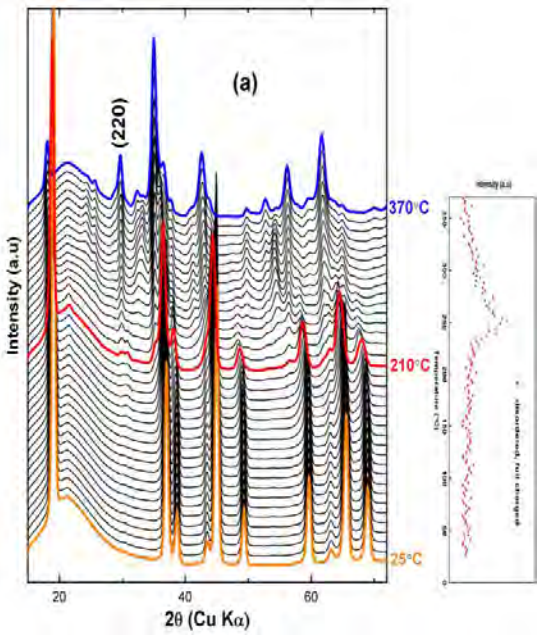


Figure 1. *In situ* XRD pattern combined with simultaneously measured mass spectroscopy (MS) data that trace oxygen gas release of fully-charged, ordered LNMO during heating up to 370°C.

Task 5.3 - PI, INSTITUTION: Clare Grey, Cambridge University

TASK TITLE: Diagnostics – NMR and Pulse Field Gradient Studies of SEI and Electrode Structure

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Capacity fade due to significant SEI formation (focusing on Si); reduced rate performance due to SEI formation; high energy density; high power

OBJECTIVE: Identify major SEI components and their spatial proximity, and how this changes with cycling. Contrast SEI formation on Si *vs*. graphite and high voltage cathodes. Correlate Li^+ diffusivity in particles and composite electrodes with rate. Investigate local structural changes of high voltage/high capacity electrodes on cycling.

GENERAL APPROACH: Multinuclear NMR of local structure; *in situ* NMR studies of Li^+ transport. Pulse Field Gradient (PFG) measurements of electrolyte diffusivity and tortuosity; SIMS and XPS of SEI composition

STATUS OCT 1, 2012: This is a new project initiated April 1, 2013.

EXPECTED STATUS SEP. 30, 2013: The ^{13}C NMR studies of the enriched carbonate electrodes will be ongoing, along with comparison studies with FEC and VC additives. Basic quantification studies of SEI formation *vs*. cycle number and depth of discharge will have been completed.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES:
(a) Identify major (NMR active) inorganic components (LiF, phosphates, carbonates) in Si SEI by NMR methods. (May 13) **On schedule**
(b) Establish viability of TOF-SIMS measurements to identify SEI components on Si. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.

TASK 5.4 - PI, INSTITUTION: Nitash Balsara, University of California, Berkeley

TASK TITLE - PROJECT: Diagnostics – Simulations and X-ray Spectroscopy of Li-S Chemistry

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: (1) Elucidating the mechanism by which the redox reactions in a sulfur cathode proceed. (2) Development of unique diagnostic tools based on X-ray spectroscopy and molecular modeling.

OBJECTIVES: A mechanistic understanding of the redox reactions and diffusion of reaction intermediates in a model sulfur cathode based on experimentally-verified models that incorporate both statistical and quantum mechanics.

GENERAL APPROACH: (1) A model Li-S cell will be built with a simple cathode comprising a binder that conducts both electrons and ions on the 10 nm length scale and sulfur nanoparticles. (2) The cells will be fabricated in a manner that facilitates the use of soft and hard X-ray spectroscopy during charge-discharge cycles. (3) Detailed (first-principles or empirical force-field) molecular dynamics simulations will be used to sample molecular configurations at finite temperature, interpret associated X-ray spectra and obtain models of (electro-)chemical reaction pathways in the cells.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. Begin measurements of X-ray spectra of polysulfides and electrolyte salts in polymer electrolytes. Begin simulations of polysulfides and electrolyte salts in polymer electrolytes that enable predicting X-ray spectra and simulate reference X-ray spectra for molecular and homogeneous condensed-phase components of interest.

EXPECTED STATUS SEP. 30, 2013: The synthesis procedure for PEDOT-PEO block copolymers that are predicted to serve as ion- and electron-conducting binders for sulfur cathodes will have been worked out. Definite spectral fingerprints of the lithiated compounds (polysulfides and salts) of interest near the absorption edges of interest (Li, O, S, C, etc.) will have been obtained.

RELEVANT USABC GOALS: Fundamental study to determine the factors that underlie limited cycle life of high energy couples such as Li-S cells.

MILESTONES:

(a) Obtain first-simulation results of molecular S_8, Li_2S_x, and Li salts in SEO PEO (or short-oligomer analogs) (Mar. 13) **On schedule**
(b) Make initial predictions of X-ray spectroscopy signatures of Li_2S_x and other components in the model Li-S cell. (Mar. 13) **On schedule**
(c) Work out the synthesis procedure for poly(dihexylpropylenedioxythiophene)-polyethylene oxide, PEDOT-PEO, (ProDOT). (Mar. 13) **On schedule**
(d) Measure X-ray spectroscopy signatures of Li_2S_x and other components in the model Li-S cell (*e.g.*, salt) in SEO and PEDOT-SEO. (Sep. 13) **On schedule**
(e) Design model Li-S cells appropriate for measurement of X-ray spectroscopy measurements as a function of state of charge of the cathode. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Milestone (a). Simulated x-ray spectra for Li_2S_x and S_8 in oligomeric polyethylene oxide (tetraglyme) have been obtained and provided in Fig. 1.

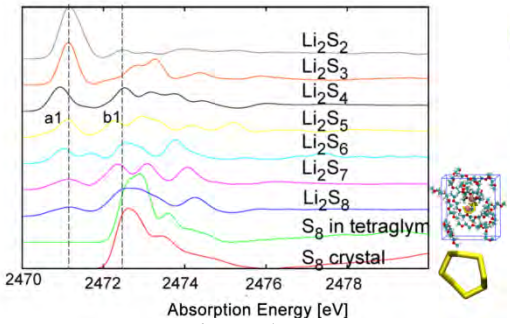


Figure 1.

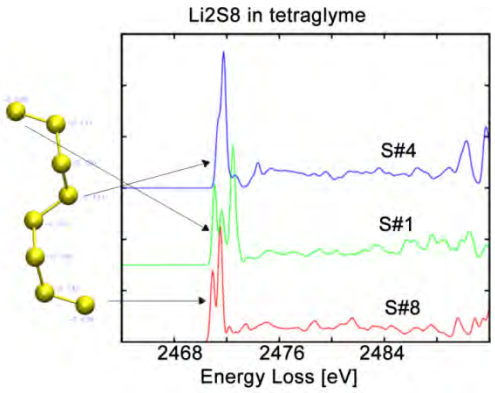


Figure 2.

Milestone (b). Theoretical results suggest that experimental spectra will have a pre-edge feature attributable to anionic polysulfide atoms (a1 in Fig. 1), and a main edge feature (b1 in Fig. 1) due to uncharged elemental sulfur. Figure 2 shows decomposition of the x-ray spectra into components that can be attributed to individual sulfur atoms in the polysulfides.

Milestone (c). A soluble electronically conducting polymer, poly(dihexylpropylenedioxy-thiophene), or ProDot, has been synthesized. Cyclic voltammetry results show an onset of oxidation around 2V *vs*. Li and maximum current flow at around 2.4V. Work to convert it into a block copolymer is underway.

Milestone (d). Measurement of x-ray spectroscopy signatures in ProDOT-PEO has not yet been attempted. However, P3HT-PEO samples with salt have been examined. Spectra obtained at ALS for LiTFSI in PEO, P3HT, and a block copolymer of P3HT-PEO can be seen in Fig. 3.

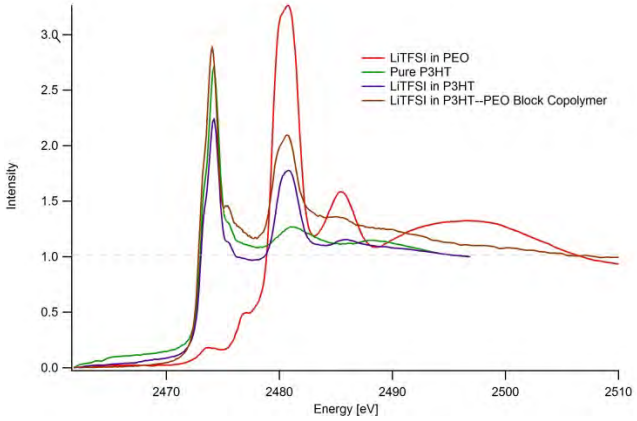


Figure 3.

Milestone (e). Work to develop batteries appropriate for *in situ* x-ray studies has not yet begun. Research has been focused on developing the library of XAS spectra needed for *in situ* experiments and on developing the ProDOT-PEO electrolyte.

Task 5.5 - PI, INSTITUTION: Jordi Cabana, Lawrence Berkeley National Laboratory

TASK TITLE: Diagnostics – Chemical and structural gradients in composite electrodes.

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, poor cycle life

OBJECTIVE: Enable higher density Li-ion batteries by informing the design of optimized electrode architectures that maximize active material utilization and charge density. Establish correlations between inhomogeneities in local states of charge, pore structure and inactive component distribution in commercially relevant electrodes. Understand the role of phase transformations within active materials vis-à-vis utilization and durability.

GENERAL APPROACH: Use spectroscopic and diffraction techniques to monitor the reactions involved in battery electrodes. Use synchrotron-based spectromicroscopy tools to probe porous composite electrodes at high chemical and spatial resolution, in 2D and 3D. Develop methodologies that rely on less sophisticated techniques to probe inhomogeneities in battery electrodes. Correlate chemical and morphological information.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. The validity of μ-X-ray absorption spectroscopy (XAS) to produce maps of local states of charge in battery electrodes has been established. Chemical tomography of particle agglomerates using full field transmission X-ray microscopy combined with XAS was established as previous work under different funding.

EXPECTED STATUS SEP. 30, 2013: *In operando* XRD will have been used to probe: i) bulk phase transformations in relevant materials and how they relate to utilization and durability, ii) the introduction of chemical gradients in NMC electrodes will have been validated. The first maps of local states of charge in commercially relevant materials will have been produced.

RELEVANT USABC GOALS: 40-mile PHEV: Energy/Weight 96 Wh/kg; CD Cycle Life 5000 cycles; Calendar Life @ 40°C 15 years.

MILESTONES:

(a) Identify, source and gather baseline electrochemical data for relevant target systems. (Mar. 13) **On schedule**

(b) Determine changes during delithiation of new fluoride and oxyfluoride phases using *in operando* bulk XRD. (Sep. 13) **On schedule**

(c) Establish the validity of using *in operando* bulk X-ray diffraction (XRD) to study the formation of chemical gradients in thick NMC composite electrodes (Sep. 13) **On schedule**

(d) Produce the first collection of chemical maps of local states of charge in composite electrodes using μ-XAS. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

This Diagnostics project was initiated late 2012. During the first weeks of award, effort has been placed on ramping up and performing the first experiments planned for FY13. Some progress toward milestones (b) and (c) has already been made. A supply of NMC electrodes from the Battaglia group have been identified and preliminary *ex situ* and *in operando* X-ray diffraction experiments have been carried out. Sourcing of other materials will still be considered in the near future. The first conclusive results will be reported in the 2nd Quarterly Report.

Collaborations this quarter: V. Battaglia, V. Srinivasan (LBNL).

Task 5.6 - PI, INSTITUTION: Guoying Chen, Lawrence Berkeley National Laboratory

TASK TITLE: Diagnostics – Design and Synthesis of Advanced High-Energy Cathode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF6+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Available energy (Goal: 11.6 kWh); Cycle life (Goal: 5,000 cycles/58 MWh).

OBJECTIVES: Obtain new insights into electrode materials by utilizing state-of-the-art analytical techniques. Gain fundamental understanding on structural, chemical and morphological instabilities during Li extraction/insertion and extended cycling. Establish and control the interfacial chemistry between the cathode and electrolyte at high operating potentials. Determine transport limitations at both material and electrode levels. Develop and synthesize next-generation electrode materials based on rational design as opposed to more conventional empirical approaches.

GENERAL APPROACH: Prepare single crystals of Li-rich layered composites and Ni/Mn spinels with well-defined physical attributes and perform advanced diagnostic and mechanistic studies at both bulk and single crystal levels. Global properties and performance of the samples will be established from the bulk analyses, while the single-crystal-based studies will utilize time and spatial-resolved analytical techniques to probe solid-state chemistry and solid-electrolyte interfacial processes at the crystallite level.

STATUS OCT. 1, 2012: This is a new project initiated October 1, 2012.

EXPECTED STATUS SEP. 30, 2013: A large collection of single-crystal samples with the layered $Li_{1+x}M_{1-x}O_2$ and spinel $LiNi_xMn_{2-x}O_4$ structures will have been synthesized. Structural, chemical, and morphological changes during first charge/discharge, particularly the activation process in the layered composites, and after extended cycling prompted deteriorated performance and stability will have been examined. Bulk and surface changes associated with metal dissolution in the active materials will have been evaluated and the dissolution mechanism examined. The impact of physical properties on these changes and subsequently the performance and stability of the oxide cathodes established. Approaches to characterize the side reaction products formed on the cathode crystal surface will have been developed.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; EV: 200 Wh/kg; 1000 cycles (80% DoD)

MILESTONES:

(a) Synthesize single-crystal samples of Li-excess layered composites and Ni/Mn spinels. (Apr. 13) **On schedule**

(b) Determine structural, chemical, and morphological changes resulting from initial Li extraction/insertion and extended cycling. Correlate these changes to crystal physical attributes. (Jul. 13) **On schedule**

(c) Evaluate transition-metal dissolution in crystal samples and examine its mechanism. (Aug. 13) **On schedule**

(d) Develop approaches to characterize the cathode-electrolyte interfacial layer. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Cathode-electrolyte interface: High-energy cathodes routinely operate at voltages above the stability window of common liquid electrolytes. Understanding and controlling the oxidation of organic solvents, dissolution of transition metals from the cathodes, and the solid-liquid interface under these conditions are therefore crucial in achieving stable cycling. To this end, micron-sized spinel $LiMn_{1.5}Ni_{0.5}O_4$ single crystals with over 90% of (112) surface facets (plates) and 100% of (111) surface facets (octahedrons) were synthesized to evaluate the influence of crystalline orientation of particle surface on interfacial reactivity. Fig. 1 shows the extended half-cell cycling performance of the crystal composite electrodes. The octahedrons delivered a higher columbic efficiency of 99% for 170 cycles, as compared to 95% for 50 cycles in the plates. The per-cycle capacity loss was 0.05 and 0.14% for the octahedrons and plates, respectively, suggesting reduced parasitic reactions on (111) crystal facets. Selected ac impedance spectra at various state of charge, measured at the OCV conditions in the potential range of 4.0 to 4.85 V, are shown in Figs. 2a and 2b. Consistent with the previous reports, the spectra from both crystal electrodes are composed of a high-frequency semicircle arise from the surface-layer resistance (R_{sf}) and capacitance (C_{sf}), a medium-to-low-frequency semicircle arise from the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}), and a low-frequency Warburg impedance (Z_w) due to solid state diffusion of Li ions within the active material. The surface-layer resistance as a function of Li content is compared in Fig. 2c. For both crystal samples, R_{sf} increased upon initial charge and then gradually decreased to reach a steady state at low Li contents, suggesting dynamic nature of the surface layer resulting from the reactions between the cathode and the electrolyte. The resistance on the octahedrons, however, is much lower compared to those on the plates. At any given Li content, the charge transfer resistance on the octahedrons is also much lower (Fig. 2d), with the difference most significant at low SOCs. The results clearly demonstrate the importance of particle morphology design in controlling side reactions of the spinels.

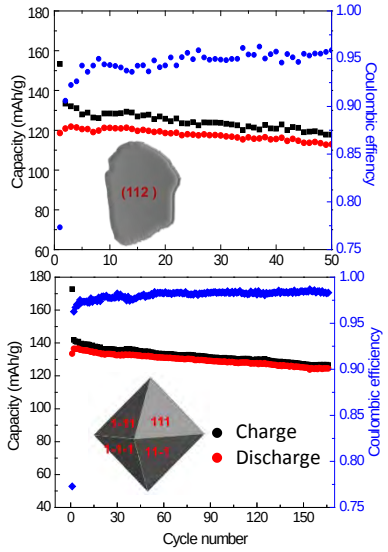


Figure 1. Half-cell cycling performance of plate (top) and octahedral (bottom) crystal electrodes.

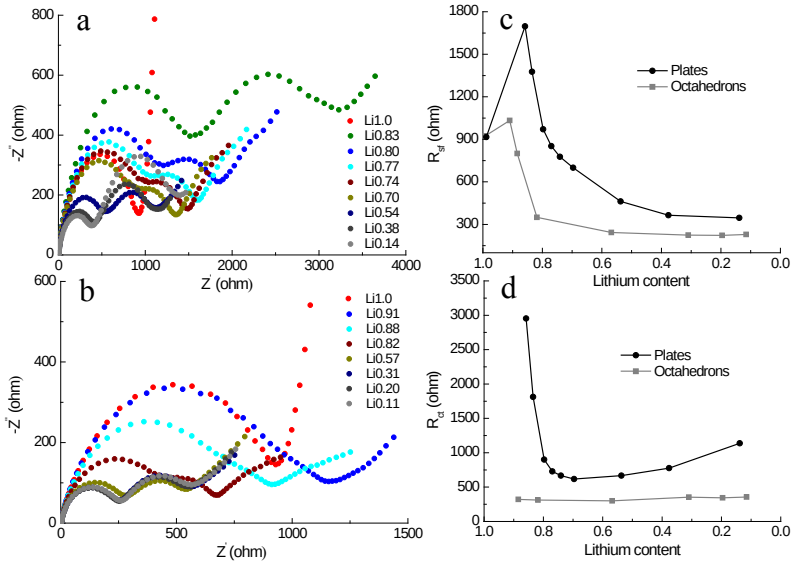


Figure 2. Nyquist plots for the crystal electrodes at the indicated Li content: a) plates and b) octahedrons; the relationships between Li content and: c) surface-layer resistance and d) charge-transfer resistance.

Collaborations this quarter: Drs. T. Richardson, J. Cabana, R. Kostecki, and M. Doeff, Profs. B. Lucht and Y.-M. Chiang, NCEM, SSRL, and ALS.

Task 5.7 - PI, INSTITUTION: Shirley Meng, University of California, San Diego

TASK TITLE: Diagnostics – Optimization of Ion Transport in High-Energy Composite Cathodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: The Li-rich oxides offer considerably higher energy density than the baseline cathode materials, but they suffer severely from the lack of lithium mobility and unstable voltage discharge profiles upon cycling.

OBJECTIVE: The ultimate goal of the proposed diagnostic work is to control and optimize Li-ion transportation, TM migration, and oxygen activity in the high-energy Li rich composite cathodes so that their power performance and cycle life can be significantly improved.

GENERAL APPROACH: The approach uniquely combines atomic resolution scanning transmission electron microscopy (a-STEM) & Electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS) and first-principles computation to elucidate the dynamic changes of the bulk and surface structural changes in the complex oxide materials during electrochemical cycling. A systematic study with powerful analytical tools is necessary to pin down the mechanisms of surface coating and determine the optimum surface characteristics for high rate and long life, and to help the synthesis efforts to produce the materials at large scale with consistently good performance.

STATUS OCT. 1, 2012: This is a new project initiated April 1, 2013.

EXPECTED STATUS SEP. 30, 2013: Establish the coherent interface between layer-layer phases and layer-spinel phases in first-principles modeling. Identify the key samples for in-depth diagnostic study by completing the electrochemical measurements. Due to the complexity of the problem, a suite of surface sensitive diagnostic tools will be applied.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; EV: 200 Wh/kg; 1000 cycles (80% DoD)

MILESTONES:

(a) Identify dynamic structure changes, quantify voltage stability upon cycling. Identify at least two best Li rich candidate materials as focused samples (among UCSD synthesized samples and other BATT teammate samples.) (Sep. 13) **On schedule**

(b) Demonstrate the chemical sensitivity and special resolution of the suite of surface characterization tools, including STEM/EELS, XPS and first-principles computation models. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.

Task 5.8 - PI, INSTITUTION: Gabor Somorjai, UC Berkeley and Philip Ross, Lawrence Berkeley National Laboratory

TASK TITLE: Diagnostics – Analysis of film formation chemistry on silicon anodes by advanced *in situ* and *operando* vibrational spectroscopy

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: High energy density Si anodes have large irreversible capacity and are not able to cycle. These failures are due in part to loss of electrolyte by reduction and an SEI that is not stable on the surface with repeated cycling.

OBJECTIVE: To understand the composition, structure, and formation/degradation mechanisms of the SEI on the surfaces of Si during charge/discharge cycles and how the properties of the SEI contribute to failure of electrochemical systems for vehicular applications.

GENERAL APPROACH: Si anode materials including single crystals, e-beam deposited polycrystalline films, and nanostructures with baseline electrolyte and promising electrolyte variations will be studied. A combination of *in situ* and *operando* Fourier Transform Infrared (FTIR), Sum Frequency Generation (SFG), and UV-Raman vibrational spectroscopies will be used to directly monitor the composition and structure of electrolyte reduction compounds formed on the Si anodes. Pre-natal and post-mortem chemical composition is identified using X-ray photoelectron spectroscopy. The Si films and nanostructures are imaged using scanning and transmission electron microscopies.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. A spectroelectrochemical FTIR cell was constructed for the Si anode system based on a previous design. The design phase of the SFG cell is on track. Control studies of SEI formation on Au films were performed using *operando* FTIR.

EXPECTED STATUS SEP. 30, 2013: Complementary *operando* FTIR and SFG studies of electrolyte reduction on Si(100) wafers and Si polycrystalline films, using the baseline electrolyte, are expected to have been conducted. At this time point Si nanostructures will have been prepared to complement the Si structures of larger dimensions.

RELEVANT USABC GOALS: EV: > 200 wH/kg with > 1000 cycles to 80 % DOD

MILESTONES:

(a) Complete construction of SFG spectroelectrochemical cell. (Jan. 13) **On schedule**
(b) Perform *operando* FTIR and SFG analyses of electrolyte reduction products on doped and undoped 100-nm thick single crystalline Si using baseline electrolyte. (May 13) **On schedule**
(c) Develop procedure to create Si thin films on current collector. (May 13) **On schedule**
(d) Perform *operando* FTIR and SFG analyses of electrolyte reduction products on at least three Si film thicknesses (*e.g.*, 10 nm, 50 nm, and 100 nm) using baseline electrolyte. (Sep. 13) **On schedule**
(e) Choose promising electrolyte additive(s) for further study to evaluate how it (they) impact the surface chemistry. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

In the first quarter, a leak-tight SFG spectroelectrochemical cell was designed and constructed to be used *in situ* and *operando* to monitor the evolution of the SEI on the Si surface. With the device, we can monitor the chemical changes on the surface without removing the Si anode from the cell. An image of the cell is shown in Fig. 1.

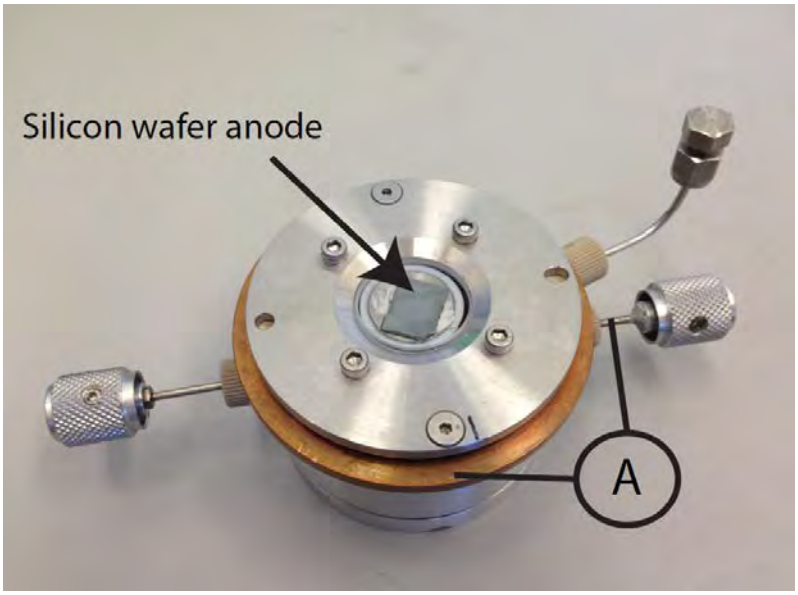


Figure 1. Image of the sum frequency generation spectroelectrochemical cell. The Si wafer anode is placed on a piston that is height-adjustable. The axle for adjusting the height and Cu plate act as a current collectors.

BATT TASK 6

MODELING

Task 6.1 - PI, INSTITUTION: Venkat Srinivasan, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling ─ Model-Experimental Studies on Next-generation Li-ion Battery Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low calendar/cycle life; Low energy, High cost

OBJECTIVES: (1) Quantify power limitations in porous cathodes and its relationship to design; (2) Measure concentration dependent transport properties of the baseline electrolyte of the BATT program [$LiPF_6$ in EC:DEC (1:1)]; (3) Quantify polarization losses at single ion conductor (ceramic) / liquid electrolyte interface; (4) Develop a model to predict the onset of mechanical damage to particle-binder interfaces in porous electrodes.

GENERAL APPROACH: Develop mathematical models for candidate Li-ion chemistries. Design experiments to test theoretical predictions and to estimate properties needed for the models. Use models to connect fundamental material properties to performance and degradation modes and provide guidance to material-synthesis and cell-development PIs. Use models to quantify the ability of the candidate chemistry to meet DOE performance goals.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. A mathematical model that accounts for the concentration and reaction distributions in the porous electrode will be developed. A simulation of a spherical particle, surrounded by a binder layer and undergoing large volume changes when charging and discharging, will be complete, and a modified kinetic expression incorporating the influence of deformation will be obtained.

EXPECTED STATUS SEP. 30, 2013: The porous-electrode model that predicts the performance of NMC cathode will be completed and compared with the experiments. Measurement of concentration dependent transport properties for the baseline electrolyte of the BATT Program [$LiPF_6$ in EC:DEC (1:1)] will be complete. Polarization losses at the single ion conductor (ceramic)/liquid electrolyte interface will be quantified. Stress calculations in 2D domains, simulating multiple interacting particles embedded in binder, will be complete.

RELEVANT USABC GOALS: *Available energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10-s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile).

MILESTONES:

(a) Measure concentration dependent transport properties (diffusion coefficient, conductivity, transference number) of $LiPF_6$ in EC: DEC (1:1 by weight); Quantify polarization losses at the single ion conductor (ceramic) / liquid electrolyte interface; Construct a simple two-dimensional system consisting of a region of active material in contact with a region of binder. Using a large-deformation intercalation model to describe the active material behavior during charge and discharge, calculate stresses at the interface between the two regions. (May 13) **On schedule**

(b) Find out baseline parameters for the porous-electrode model and compare the model results with experimental data to understand solution-phase limitation; Quantify the rate of side reactions for NMC cathodes and extract kinetic parameters; Use the large-deformation model to approximately represent a system of particles dispersed in a binder matrix, calculating stresses throughout the system. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Cycling lithium in a Li-Li symmetric cell: Lithium metal is frequently used as the anode in all research half-cells and cycling of Li-Li symmetric cells remains ubiquitous. However, the potential of Li is unstable (See red line in Fig. 1) making interpretation of data difficult. Over the last quarter, a "formation" protocol was established that leads to stable cycling (blue line in Fig. 1). This protocol will be used in all Li measurements, including transport properties, in the future.

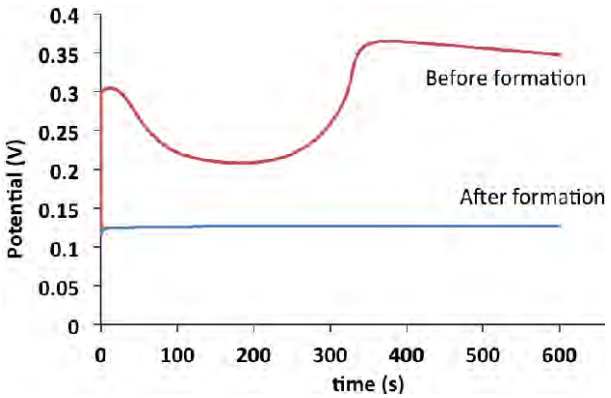


Figure 1. Potential profile of a Li-Li symmetric cell at 0.28 mA/cm^2 for 1M $LiPF_6$ in EC:DEC (1:1) before and after formation cycles.

Ion Transport in liquid electrolytes: Measurement of transport properties (diffusion coefficient, conductivity, transference number) of organic electrolytes as a function of concentration (up to 2M) remains an important area of exploration because of the lack of good experimental data. A diffusion cell has been designed to measure these properties of $LiPF_6$ in EC: DEC (1:1 by weight) using restricted diffusion and galvanostatic polarization methods. For diffusion coefficient measurements, constant current is passed for certain time, which builds up a concentration gradient in a Li-Li cell. Current is then stopped and cell potential is monitored. At long times the slope of ln V *vs*. time curve is proportional to the salt diffusion coefficient at that particular electrolyte concentration. Initial results for 0.2M and 1M suggest that the diffusion coefficient values obtained using restricted diffusion are higher by one and two orders of magnitude, respectively from those measured by using UV-vis absorption. Future work will focus on alternate ways, such as reference electrode and limiting current experiments, to crosscheck the diffusion coefficient values obtained using the restricted diffusion method.

Understanding mechanical degradation in Si anodes: The large-deformation single-particle model of Christensen and Newman (2006) will be used as a basis for simulations of simple model systems combining active material and a binder/conductive additive composite. Solutions have previously been obtained for spherically-symmetric particles, but solutions in 2D domains should show a richer variety of mechanical interactions. The equations are challenging to solve; solutions could not be obtained with a commonly-used commercial numerical simulation package. Available open-source packages are either too inflexible or require programming in languages that are uncommon in the community. To address these difficulties, a numerical package for the Python programming language is being developed. This will allow discretized equations to be represented in a relatively simple but very detailed way. It has already been used to solve systems of simple differential equations on 2D domains, and it is hoped that this approach will soon provide solutions for the full model of Christensen and Newman. This library will first be used to calculate stresses in a model system, consisting of a cylindrical disk of active material undergoing a charge/discharge cycle with the assumption that the material remains undamaged. Comparison of the computed stresses with yield stress measurements, where available, and should indicate whether damage is likely to occur under the simulated conditions. This simulation will then be extended by placing active material in contact with a binder/conductive material, as required by the May milestone.

Task 6.2 - PI, INSTITUTION: Kristin Persson, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling – Predicting and Understanding Novel Electrode Materials From First-Principles

SYSTEMS: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: High cost, low energy, low rate, poor cyclability.

OBJECTIVES: 1) Understand the atomistic mechanisms underlying the behavior and performance of the Li-excess as well as related composite cathode materials underlying, and 2) make recommendations for modifications to mitigate voltage and capacity fade.

GENERAL APPROACH: First-principles atomistic simulations and statistical mechanics approaches will be used to study the thermodynamic and kinetic processes that govern the electrochemical behavior of the lithium excess and related composite layered-layered or layered-spinel materials. Phase stability, defect formations in the Li, oxygen and cation lattices will be studied, as well as the migration paths for the mobile species.

STATUS OCT. 1, 2012: New project initiated October 1, 2012. First-principles calculations utilized to map out the layered Li_2MnO_3 (LMR), layered $LiMnO_2$ and $LiMn_2O_4$ phase diagrams, and structures including defect cation compositions to yield the possible stable and metastable delithiation and lithiation paths from the first charge and onwards. This will yield an understanding of the thermodynamically accessible phase space as a function of the oxygen release and possible cation rearrangements.

EXPECTED STATUS SEP. 30, 2013: Comprehensive phase diagrams as function of Li, O, Mn and defect (vacancies) in layered and spinel (defect) structures to inform on the stability as a function of SOC.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade

MILESTONES:

(a) Phase diagram including relevant bulk Li, O and Mn and defect phases in layered Li_2MnO_3. (Jun. 13) **On schedule**
(b) Phase diagram including relevant bulk Li, O and Mn and defect phases in layered $LiMnO_2$ (Sep. 13) **On schedule**
(c) Phase diagram including relevant bulk Li, O and Mn and defect phases in spinel $LiMn_2O_4$ (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

Collaborations: Prof Gerbrand Ceder (MIT), Dr. Jordi Cabana (LBNL), Guoying Chen (LBNL), Clare Grey (U Cambridge, UK).

While the high-voltage spinel work has concluded, work on the Li_2MnO_3 system is ramping up. This report gives the latest results for the $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO), which have been submitted for publication. For many systems, nano-scaling of electrode materials is frequently used in battery applications to enhance performance, particularly concerning rate capability. However, for the high-voltage spinel, LNMO, conflicting results have been reported on the effectiveness of nano-scaling to enhance its rate performance. In this study, first-principles calculations were performed to investigate the effect of nano-scaling on LNMO, specifically focusing on the role of surface stability and cation ordering. Surface energy was calculated and compared for the low index facets (100), (110), and (111), and it was found that the most stable facet is dependent on the cation ordering at the surface layer.

For a uniformly disordered structure (the most highly occurring local ordering in the disordered spinel with random cation arrangements), the (111) facet has the lowest surface energy among the investigated facets, which agrees with several existing experimental observations. For the ordered structure, however, using only the atomic rearrangement required to remove the dipole moment and routine cell relaxations, the (100) facet with the Li/Mn/Ni/O-termination is predicted to be most stable, which contrasts with experimental observations. Surface reconstruction, previously found to be successful for the $LiMnO_2$ spinel (Karim and Persson, PRB 2013), was applied. The findings showed that the (111) facet can be drastically lowered if a targeted surface reconstruction is employed where the Mn ions on the surface are locally swapped with the Li ions in the next available layer leading to an inverse spinel structure near the surface. This reconstruction successfully rendered the (111) facet the most stable for the LMNO ordered system, as expected for the spinel structure. In summary, our calculations predict that the (111) facet is the most stable surface facet (followed by the (100) and the (110) facets), for both the ordered as well as the disordered LMNO materials, resulting in the equilibrium cubo-octahedral particle morphology. The surface reconstruction in the ordered material results in a deviation from the ideal ordered surface cation arrangement, which will likely result in an enhanced accessibility to the Li-vacancy solid-solution region close to the surface.

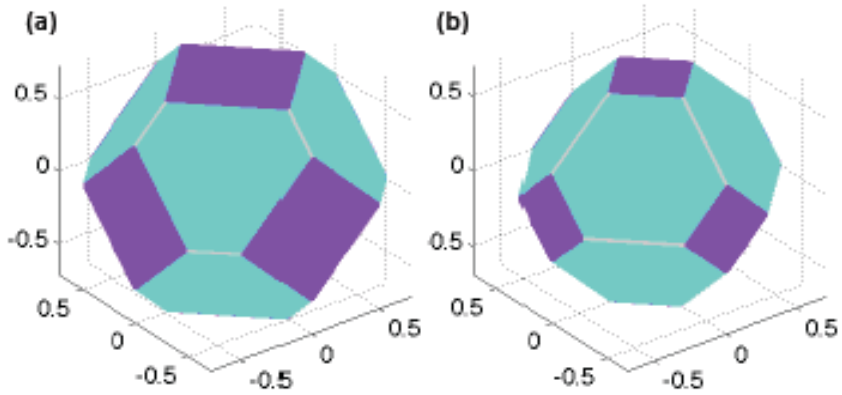


Figure 1. The equilibrium shape of (a) the ordered spinel structure with a local inverse spinel (b) the disordered spinel structure. The (100), (110), and (111) facets are colored violet, grey, and turquoise, respectively.

Task 6.3 - PI, INSTITUTION: Gerbrand Ceder, Massachusetts Institute of Technology

TASK TITLE: Modeling – First Principles Calculations of Existing and Novel Electrode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low rate capabilities; high cost; poor stability; low energy-density

OBJECTIVE: Develop more stable high capacity Li-excess layered cathodes. Develop high-capacity, high-rate Na-intercalation electrodes. Generate insight into the behavior of alkali-intercalating electrode materials.

GENERAL APPROACH: Use first-principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, mobility of Li- and transition-metal ions, and the effect of structure on rate capability. Anticipate possible instabilities in materials at high states of charge by using calculations.

STATUS OCT. 1, 2012: This is a new project initiated April 1, 2013.

EXPECTED STATUS SEP. 30, 2013: Models for Li transport in partially disordered Li-excess NMC materials will have been initiated. The phase diagram calculation of this material will have been started by studying the ground states of the Li-Ni-Mn-O and Li-Co-Mn-O system. An understanding of what determines the structure selection of Na_xMO_2 materials and its effect on rate will be reached.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade

MILESTONES:
(a) Obtain relative stability of Na_xMO_2 materials in different structures: P2, P3, O3, O2 for M = single metal (Jun. 13) **On schedule**
(b) Understand Na mobility difference between P2 and O3 structures (Sep. 13) **On schedule**
(c) Obtain ground state structures in the Li-Co-Mn-O and Li-Ni-Mn-O system covering layered, spinel, and the known ternary compounds in this space. (Sep. 13)
(d) Initiate model study to understand Li transport in overcharged Li-excess materials. (Sep. 13)

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.

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Task 6.4 - PI, INSTITUTION: Perla Balbuena, Texas A&M University

TASK TITLE: Modeling – First-principles Modeling of SEI Formation on Bare and Surface/additive Modified Silicon Anode

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Modeling different surface terminations; characterization of electron transfer through the SEI layer; description of SEI structure and evolution.

OBJECTIVE: Develop fundamental understanding of the molecular processes that lead to the formation of a SEI layer due to electrolyte decomposition on Si anodes, and use such new knowledge for a rational selection of additives and/or coatings.

GENERAL APPROACH: Focus is placed SEI layer formation and evolution during cycling and subsequent effects on capacity fade using two models: 1) SEI layers on bare Si surfaces, and 2) SEI layers on coated surfaces. Reduction reactions will be investigated with quantum chemistry (cluster-based) calculations on simplified models of electrodes; static ultra-high vacuum type DFT calculations of model electrodes with one electrolyte solvent/salt molecule; ab initio molecular dynamics simulations of the liquid-solid interface; and ab initio-Green's function theories to evaluate rates of electron transfer.

STATUS OCT. 1, 2012: This is a new project initiated on April 1, 2013.

EXPECTED STATUS SEP. 30, 2013: Most stable Li_xSi_y surfaces will have been identified and adsorption of most common solvents characterized. Adhesion of common surface oxides (*i.e.,* SiO_2, Li_4SiO_4) on Li_xSi_y surfaces and reactivity of the composite surface will be evaluated. Assessment of electron transfer through simple models of SEI layers on model electrodes; surface effects on reduction reactions of EC, VC, FEC, including solvation effects characterized through cluster models, will be carried out.

RELEVANT USABC GOALS: Additives/coatings for improved SEI layers in Si anodes.

MILESTONES:

(a) Identify most favorable surfaces of bare Li_xSi_y periodic structures and characterize their reactivity. (Jun. 13) **On schedule**
(b) Characterize geometric, electronic, and Li^+ transport properties of surfaces coated with thin layers of SiO_2 and Li_4SiO_4 oxides. (Sep. 13) **On schedule**
(c) Estimate maximum SEI layer thickness for electron transfer in model SEI films. (Jun. 13) **On schedule**
(d) Characterize surface effects on EC, VC, FEC decomposition using cluster models of bare Li_xSi_y structures. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.

Task 6.5 - PI, INSTITUTION: Yue Qi, General Motors

TASK TITLE: Modeling ─ A Combined Experimental and Modeling Approach for the Design of High Current Efficiency Si Electrodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low calendar and cycle life; low current efficiency, high cost

OBJECTIVE: Combine modeling and experimental approaches to understand, design, and make stabilized nanostructured Si anode with high capacity and high coulombic efficiency.

GENERAL APPROACH: In this project, four coherent steps will be taken: a) Develop a multi-scale model to predict the stress/strain in the SEI layer (including artificial SEI) on Si and establish a correlation between the capacity loss (or current efficiency) and mechanical degradation of SEI on Si; b) Use atomic simulations combined with experiments to provide critical material properties used in the continuum modeling; c) Investigate the impact of the SEI formation on the stress/strain evolution, combined with modeling to quantify the current efficiency related to a variety artificial SEI layers using *in situ* electrochemical experiments; d) Use the validated model to guide surface-coating design and Si size/geometry optimizations that mitigate mechanical degradation to both SEI and Si.

STATUS OCT. 1, 2012: This is a new project initiated on May 1, 2013. Collaboration between all CoPIs: Yue Qi (GM), Xingcheng Xiao (GM), Huajian Gao, (Brown U), Brian W. Sheldon (Brown U), and Yang-Tse Cheng (U. of Kentucky) has been established.

EXPECTED STATUS SEP. 30, 2013: In phase one of this project some key mechanical and electrochemical properties of non-coated and coated Si thin-film electrode will be determined.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

(a) Determine the elastic properties of artificial SEI on Si (including Li_xCO_3, AlO_x, SiO_x) *via* both atomic modeling and laser acoustic wave measurements. (May 13) **On schedule**
(b) Correlate the interfacial charge-transfer kinetics and coating thickness on Si film electrode. (Jun. 13) **On schedule**
(c) Evaluate the chemical composition of the initial SEI formed on uncoated Si thin-film electrodes. (Aug. 13) **On schedule**
(d) Evaluate the evolution of stress and surface roughness of the Si electrode during SEI formation and growth in *in situ* cells to inform the continuum stress model. (Sep 13) **On schedule**
(e) Formulate a theoretical framework to connect mechanical degradation and columbic efficiency. (Sep. 13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on May 1, 2013.

Task 6.6 - PI, INSTITUTION: Dean Wheeler and Brian Mazzeo, Brigham Young University

TASK TITLE: Modeling ─ Predicting Microstructure and Performance for Optimal Cell Fabrication

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cell performance, life, cost

OBJECTIVES: Develop rapid, reliable, and standardized methods for measuring electronic and ionic conductivities in porous electrodes. Determine and predict microstructures for porous electrodes. Understand tradeoffs and relationships between fabrication parameters and electrode performance.

GENERAL APPROACH: Use particle-based microstructural modeling, coupled with extensive experimental validation and diagnostics, to understand relationships between fabrication processes, microstructure, and corresponding electron and ion transport in composite electrodes. Assess electronic and ionic conductivities of porous electrodes attached to current collectors, including local heterogeneities and anisotropic effects, through the use of newly-designed instrumentation. Validate and parameterize the particle model using experimental microstructural and macroscopic properties. Use modeling and diagnostic tools to suggest processing conditions that will improve cell performance.

STATUS OCT 1, 2012: This is a new project initiated on April 1, 2013. Plans to accomplish the above objectives over a 4-year period are in place.

EXPECTED STATUS SEP. 30, 2013: Micro-four-line probe will have been fabricated and the utility of the measurement technique will have been demonstrated on laboratory-prepared and commercial films.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years.

MILESTONES:

(a) Fabricate first-generation micro-four-line probe to determine bulk electronic conductivity in non-delaminated battery films. (Sep. 13) **On schedule**

(b) Develop mathematical-model inversion technique to determine current collector contact resistance from film measurements. (Sep.13) **On schedule**

PROGRESS TOWARD MILESTONES

The project was awarded under the 2012 RFP and will officially start on April 1, 2013.